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Vinyl Fluoride

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The review deals with the methods of preparation, physical and chemical properties, and polymerisation and copolymerisation of vinyl fluoride with various unsaturated compounds as well as the properties, stabilisation, processing, and applications of its polymers and copolymers based on the data published up to the end of 1968.
The bibliography includes 299 references.

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I. INTRODUCTION

Numerous studies dealing with the synthesis, polymerisation, and copolymerisation of vinyl fluoride have been published. Polymers and copolymers of vinyl fluoride are of great interest because they have many valuable properties: high thermal stability, resistance to the action of light, chemical reagents, and radiation, and exceptional resistance to weathering.

Certain results of studies dealing with vinyl fluoride were described in the 1951 review by Knunyants and Fokin[1] on the polymerisation of fluoro-olefins and in a later monograph by Vaculik[2] on the chemistry of monomers.

II. METHODS OF PREPARATION OF VINYL FLUORIDE

Vinyl fluoride (VF) was obtained for the first time by Swarts[3,4] in 1901:

$$BrCH_2{-}CHBr_2 \xrightarrow[100,180^\circ]{SbF_3,Br_2} \begin{cases} \rightarrow BrCH_2{-}CHF_2 \\ \rightarrow BrCH_2{-}CHBrF \end{cases} \xrightarrow[C_2H_5OH]{Zn} H_2C{=}CHF$$

Later he synthesised it[5] in 98% yield from 1,1-difluoro-2-iodoethane:

$$F_2CH{-}CH_2I \xrightarrow[ether]{C_6H_5MgBr} H_2C{=}CHF\ .$$

1. Preparation of Vinyl Fluoride by Hydrofluorination of Acetylene

Investigators have devoted most attention to the synthesis of vinyl fluoride by the hydrofluorination of acetylene. In the absence of a catalyst and high pressures vinyl fluoride is not formed at temperatures ranging from −70° to 0°C[6]. The possibility in principle of obtaining vinyl fluoride from acetylene and hydrogen fluoride under pressure was mentioned in patents as early as the 1920's[7], but the process itself was achieved much later by Grosse and Linn[6] with a conversion of acetylene of about 15%:

$$HC{\equiv}CH \xrightarrow[20^\circ,72\ h]{8-12\ atm} H_2C{=}CHF + CH_3{-}CHF_2\ .$$

The catalytic method is more effective. A number of catalysts have been proposed for the vapour-phase process, among which mercury compounds have become most widely known: HgO and $HgCl_2$ on activated charcoal[8], in the presence of hydrogen chloride[9] or hydrogen chloride and iron(III) chloride[10]. Newkirk[11], who used as catalyst mercury(II) chloride on activated charcoal promoted with barium chloride, obtained an 82% yield of vinyl fluoride at 97−104°C. Under the same conditions in the absence of barium chloride, the yield of vinyl fluoride fell to 51.5%. Dolgopol'skii et al.[12] used HgO in liquid paraffin as a catalyst. Acetylene was passed through a vessel with anhydrous hydrogen fluoride and then through a suspension of HgO in liquid paraffin. At 0°C, for a molar ratio $C_2H_2:HF = 1:3.48$ and an acetylene flow rate of 6 litre h^{-1}, the yield of vinyl fluoride was 68.4%. Using mercury acetate on activated charcoal at 40°C and a molar ratio $C_2H_2:HF = 1:1.5$, it proved possible to obtain vinyl fluoride in 86% yield[13]. Other mercury compounds on activated charcoal have also been used as catalysts, for example nitrates[14-17] (at temperatures between 0° and 100°C). Apart from activated charcoal, alumina, graphite[17], or solid organic polymers[16,17] can be used as carriers, which stabilise the catalyst and increase the duration of its activity. A method of preparation of vinyl fluoride in the presence of mercury salts on activated charcoal at 30−40°C in a polypropylene reactor has been described. The catalyst functioned for 240 h without loss of activity[18].

It has been noted that at an elevated temperature activated charcoal reduces mercury salts and deactivates them. The mercury thus produced evaporates and condenses in various parts of the apparatus. Loss of mercury also leads to a decrease of the activity of the catalyst and in addition results in the formation of mercury fluoride, which induces the polymerisation of vinyl fluoride. To prevent the reduction of mercury salts, iron(III) salts or other oxidants are added to the catalyst, which increases its activity and duration of its useful operational life[11].

Mercury nitrate deposited on alumina in an amount of 5−20 wt.% proved to be a long-lived catalyst for the synthesis of vinyl fluoride. After passing a mixture of 48% of acetylene, 50% of hydrogen fluoride, and 2% of nitrogen oxides through the catalyst at 65°C and neutralising

the product, a mixture of 66% of vinyl fluoride and 34% of 1,1-difluoroethane was obtained[17]. Zinc and mercury chromates[19] or mixtures of mercury, zinc, and nickel chromates[20] have also been used as catalysts at temperatures in the range 75–250°C. Boric acid was added to prevent the sintering of the catalyst[19].

The synthesis of vinyl fluoride at 20–100°C with catalysts consisting of mercury(II) oxide on activated charcoal or alumina and also TiO_2 or ZrO_2 on the same carriers, subjected to preliminary irradiation or irradiated during the reaction with γ-rays, has been described[21,22]. The yield of the monomer was 70%.

When activated alumina or aluminium trifluoride were used as catalysts at temperatures in the range 250–400°C, a mixture of vinyl fluoride and 1,1-difluoroethane was obtained[23-28]. The same compounds were synthesised in the presence of aluminium sulphate[29] or a 3:1 mixture of Al_2O_3 and ZnF_2.[30]

Skiles proposed zinc[31] and chromium[32] catalysts. In the first case the catalyst was prepared by mixing zinc oxide with cane sugar in water and the resulting paste was dried and carbonised at 700°C.

Clark[33] obtained vinyl fluoride in the presence of copper cyanide deposited on activated charcoal or other porous carriers inert with respect to hydrogen fluoride. When copper chloride on activated charcoal was tested, the conversion of acetylene was only 0.3%.

The use of fluorosulphonic acid as a catalyst for the hydrofluorination of acetylene has been reported. At 0°C 1,1-difluoroethane forms in 85% yield and at 80–90°C the product is a mixture of 50% of vinyl fluoride and 40% of 1,1-difluoroethane[34]. Linn[35] obtained vinyl fluoride in the presence of boron trifluoride.

With cadmium sulphate, nitrate, or acetate on activated charcoal in a stationary or fluidised bed as catalysts, vinyl fluoride was obtained in 98% yield at 300°C. The catalysts functioned for 50 h without loss of activity. The vinyl fluoride contained traces of acetylene and 1,1-difluoroethane[36].

When the catalyst was aluminium trifluoride with a small amount of BiF_3 or $Bi(OH)_3$, a mixture of 70.3% of vinyl fluoride and 29.6% of 1,1-difluoroethane was obtained at 200–400°C; the conversion of acetylene was 96.7%[37]. Since vinyl fluoride and acetylene have similar boiling points, there are technical difficulties in the isolation of the pure monomer free from acetylene. McMillan[38] purified vinyl fluoride by azeotropic fractionation of the mixture using ethane, which forms an azeotrope with acetylene. Kalb et al.[39] separated vinyl fluoride from 1,1-difluoroethane, hydrogen fluoride, and other impurities by distillation. Traces of hydrogen fluoride were removed by passing the monomer through columns filled with sodium carbonate and acetylene was removed by washing the monomer in a scrubber with an ammoniacal solution of copper(I) chloride. Oxygen was removed by repeated distillation at a pressure of 2.8–7 atm at temperatures ranging from −50° to −25°C.

For the removal of acetylene from vinyl fluoride, dimethyl sulphoxide and dimethylformamide or their mixtures[40] as well as *N*-methylpyrrolidinone[41] were proposed as selective solvents for acetylene. It has also been suggested that a mixture of vinyl fluoride, acetylene, and 1,1-difluoroethane be brominated at 0°C with subsequent distillation of the bromination products; pure vinyl fluoride was obtained by treating 1,2-dibromo-1-fluoroethane with zinc in alcohol[42]. The purification of vinyl fluoride by the hydrochlorination of the acetylene impurity with subsequent fractionation of the mixture is very promising[43]. Usmanov et al.[44] developed a method for a high degree of elimination of acetylene and difluoroethane from vinyl fluoride in a gas saturator with glass frit gas spreaders consisting of 5 saturators connected in series and two gas-absorption columns. Acetylene was absorbed in a solution of ammonium chloride and copper(I) chloride in aqueous ammonia. The gas flow rate was maintained in the range 10–15 litre h^{-1}. This method made it possible to reduce the acetylene content in the crude monomer to 4×10^{-5}%. Difluoroethane was removed from vinyl fluoride on a column for low-temperature fractionation. The purified monomer contained not more than 1×10^{-4}% of difluoroethane.

2. Preparation of Vinyl Fluoride by the Dehydrofluorination of 1,1-Difluoroethane

Vinyl fluoride has been obtained[45-47] by the pyrolysis of 1,1-difluoroethane at 350–1000°C and in the presence of activated charcoal at 300–600°C:

$$CH_3{-}CHF_2 \xrightarrow{-HF} H_2C{=}CHF \ .$$

Pyrolysis of 1,1-difluoroethane in the presence of 2% of oxygen at 500°C gave a 61% yield of vinyl fluoride[48]. Calcium fluoride, charcoal, and steel filings were used as catalysts at 300–600°C, the yields of vinyl fluoride being 75, 84, and 88% respectively[49]. Vinyl fluoride forms in 32.7% yield at 400–850°C in the presence of a catalyst based on $CrF_3.H_2O$. Without the catalyst, the amount of acetylene increased and the conversion fell to 3.3%[50].

By dehydrofluorinating 1,1-difluoroethane on activated charcoal at 350°C, a mixture containing 27.8% of vinyl fluoride and 62.7% of 1,1-difluoroethane was obtained; at a reaction temperature of 400°C the amount of vinyl fluoride rose to 37.2%[51]. 1,1-Difluoroethane has also been pyrolysed in a steel tube on charcoal or metals and their oxides and salts of Groups I, II, V, and VII,[52,53] at 300–800°C. The yield of vinyl fluoride reached 88%. When 4–6% of nickel oxide on alumina was used as a catalyst at 400°C, the yield of vinyl fluoride rose to 99%[54].

By passing a 1.7:1 mixture of 1,1-difluoroethane and acetylene over aluminium trifluoride at 250–300°C, a mixture containing 64% of vinyl fluoride, 1.6% of acetylene, 0.3% of ethylene, and 1.1% of hydrogen fluoride was obtained. Unsaturated hydrocarbons were removed by catalytic hydrogenation (in the presence of palladium on charcoal) in the form of ethane and vinyl fluoride was isolated by fractional distillation[55].

3. Other Methods for the Preparation of Vinyl Fluoride

Henne and Midgley[56] synthesised vinyl fluoride by treating 1,2-dichloro-1-fluoroethane with zinc in alcohol. Vinyl fluoride forms in 50% yield from 1,1-difluoro-2-iodo- or 1,2-dibromo-1-fluoro-ethane on treatment with magnesium, sodium, or potassium in ether[57]. Benning et al.[58] suggested acetone, pyridine, and dioxan, in addition to alcohol, as the medium for the elimination of halogen atoms with zinc.

Vinyl fluoride was synthesised in 58% yield from 1-chloro-2-fluoroethane by the elimination of hydrogen chloride with soda-lime at 400°C[59]. A high yield of vinyl fluoride in the pyrolysis of 1-chloro-1-fluoroethane at 500–800°C at a reduced pressure[47,60], in a chromenickel tube[61] and in the presence of copper or Cu_2Cl_2 powder[62], has been reported. In the last case the yield was 97.9%.

The fluorination of alkyl halides with hydrogen fluoride at an elevated temperature and pressure on activated charcoal[63] or alumina[64] is accompanied by the elimination of hydrogen halides and the formation of vinyl chloride and fluoride. The latter was also isolated in the pyrolysis of 1,2-difluoroethane on alumina, calcium sulphate, or activated charcoal at 200–400°C [65]. A mixture of ethyl and vinyl fluorides was obtained from ethane on oxidative fluorination in the presence of iron(III) oxide or lead oxide at 325–700°C [66]. The products of the fluorination of ethylene with mercury(II) fluoride at 150–180°C in an autoclave are hexafluoroethane and vinyl fluoride[67]. Vinyl fluoride has also been synthesised from ethylene, hydrogen fluoride, and oxygen, using as a catalyst a mixture of $PdCl_2$, $FeCl_3$, and $CuCl_2$ on activated charcoal[68]. The formation of vinyl fluoride by the reaction of ethylene and alkali metal fluorides in the presence of $PdCl_2$ in an autoclave at 160–190°C has been described; the reaction medium may be benzonitrile, nitrobenzene, dibutyl phthalate, or tetrahydrofuran (THF)[69,70]. After being passed over a Cr_2O_3 catalyst on alumina at 300–400°C, a mixture of 1,2-dichloroethane and hydrogen fluoride was found to contain about 20% of vinyl fluoride[71]. Vinyl fluoride forms in 70% yield when fluorine reacts with a complex of vinylmagnesium chloride and tetrahydrofuran[72].

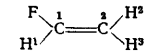
By passing vinyl chloride through a vessel with anhydrous hydrogen fluoride in the presence of oleum at a temperature not exceeding 20°C, a mixture of vinyl chloride, 1-chloro-1-fluoroethane, 1,1-difluoroethane, and hydrogen chloride and fluoride was obtained; this was then pyrolysed at 400–800°C. The gas from the pyrolysis was passed through a fractionating column, where hydrogen chloride and vinyl fluoride were separated and a mixture of hydrogen fluoride, vinyl chloride, and fluoroethanes was returned to the hydrofluorination reactor. The vinyl fluoride did not contain acetylene as an impurity; the yield was 85%[73]. Vinyl fluoride forms when vinyl chloride reacts with a fluorinated anion-exchange resin in the presence of a palladium salt in acetic or propionic acid, tetrahydrofuran, or dimethylformamide at 0–200°C [74]. Vinyl fluoride has been isolated in the photolysis of 1,3-difluoroacetone[75].

III. PHYSICAL PROPERTIES OF VINYL FLUORIDE

At normal temperatures and pressures vinyl fluoride is a colourless gas with a boiling point of −72.2°C, a melting point of −160.5°C, and $d_4 = 0.853$ at −72.2°C. It is insoluble in water and is relatively sparingly soluble in alcohol and acetone[8]. It has not been found to have a narcotic effect[76]. The heat of formation ($-\Delta H$) of vinyl fluoride from the elements in the gaseous state at 25°C has been calculated as +28 kcal mole^{-1}.[7] The experimental dipole moment is $\mu = 1.42 \pm 0.01$ D.[78] The ionisation potential of vinyl fluoride, determined by photoionisation and electron impact methods, has been found to be 10.37 and 10.45 eV respectively[79–82].

In recent years spectroscopic methods have been widely used to study vinyl fluoride. The vibration spectra have been investigated by many workers[83–95], who used them largely to determine and describe the geometrical structure of the vinyl fluoride molecule. A full compilation of all the geometrical parameters is presented in Table 1. The infrared spectrum of vinyl fluoride was obtained for the first time by Torkington and Thompson[92]. Bak and Christensen[94] analysed the infrared spectra of vinyl fluoride and all seven of its deutero-derivatives and assigned the frequencies of the fundamental vibrations of the molecules. The isotopic compounds were isolated from the mixture and freed from non-isotopic admixtures on silica gel at 43°C, the purity of the compounds obtained being checked by infrared spectroscopy. Sverdlov et al.[91] achieved a complete interpretation of the vibration spectra of vinyl fluoride and its deutero-derivatives.

Table 1. Bond lengths (Å) and valence angles in the vinyl fluoride molecule



Bonds and angles	Method		
	microwave spectroscopy Ref.83	microwave spectroscopy, least squares method (Ref.84)	isotopic shift method (Ref.85)
C_1-F	1.348	1.344±0.002	1.347±0.009
C_1-H_1	1.073	1.080±0.005	1.082±0.004
C_2-H_2	1.080	1.075±0.005	1.077±0.003
C_1-C_2	1.333	1.337±0.002	1.329±0.006
C_2-H_3	—	—	1.087±0.003
FC_1H_1	115.4°	—	110.0±1°
$H_1C_1C_2$	123.7°	—	—
$H_2C_2C_1$	121.1°	—	120.9±0.3°
$H_3C_2C_1$	118.5°	—	119.0±0.3°
C_2C_1F	—	121±0.2°	120.8±0.3°

Quite recently the NMR spectra[96–103], electronic spectra[82], and mass spectra[81] of vinyl fluoride were reported. The values and relative signs of the spin–spin interaction constants and chemical shifts have been determined and it has been shown that the variation of the latter with the electronegativity of the atoms is close to linearity. Fogg and Lambert[104] studied the propagation of ultrasonic waves in vinyl fluoride at 100°C.

IV. ANALYSIS OF VINYL FLUORIDE

Newkirk[11] determined the density of gaseous vinyl fluoride on an Edwards balance and measured its amount by absorption in bromine water. Of the modern analytical methods, gas chromatography[44,105,106] and infrared spectroscopy[92] may be used. The analysis of the mixture consisting of 1-chloro-1-fluoroethane, 1-chloro-2-fluoroethane, and vinyl fluoride on a laboratory chromatograph of type KhL-3 has been described[105]. A mixture of trifluoromethane, chlorotrifluoromethane, 1,1-dichloro-2,2-difluoroethylene, vinyl fluoride, nitrogen, and oxygen has been separated[106]. Usmanov et al.[44] have proposed a method of analysis by gas–liquid chromatography with a flame-ionisation detector on a column with 25% of liquid paraffin on an INZ-600 carrier as the stationary liquid phase.

V. CHEMICAL PROPERTIES OF VINYL FLUORIDE

Reactions involving the double bond of vinyl fluoride have ionic and radical mechanisms. Reactions of the first type include the addition of halogens[3,42] and hydrogen halides, the latter following the Markovnikov rule with the exception of hydrogen bromide under the conditions of a

radical process[107]. Hydrogen fluoride adds to vinyl fluoride with greater difficulty than to unsubstituted ethylenes, which can be accounted for by the effect of the highly electronegative fluorine atom. The addition of hydrogen fluoride to vinyl fluoride is catalysed by the halides of certain metals and also by fluorosulphonic acid[34]. Yakubovich et al.[108,109] showed that nitrosyl chloride adds to vinyl fluoride with formation of 1-chloro-1-fluoro-2-nitrosoethane, which is then oxidised to 1-chloro-1-fluoro-2-nitroethane:

$$H_2C{=}CHF + NOCl \rightarrow [FClCH{-}CH_2NO] \rightarrow FClCH{-}CH_2NO_2 .$$

The reaction of vinyl fluoride with thioacetic acid under irradiation with ultraviolet light and in the presence of benzoyl peroxide[110] gave a 75% yield of 2-fluoroethyl thioacetate:

$$CH_3{-}C(=O){-}SH + H_2C{=}CHF \xrightarrow[3\ h]{h\nu} CH_3{-}C(=O){-}S{-}CH_2{-}CH_2F .$$

Yarovenko and Vasil'eva[111] obtained a 30% yield of di(2-chloro-2-fluoroethyl) sulphide by irradiating with ultraviolet light a mixture of copper(I) chloride and vinyl fluoride under pressure in the presence of benzoyl peroxide for 200 h at 20°C[111]:

$$H_2C{=}CHF + S_2Cl_2 \xrightarrow{h\nu} S(CH_2{-}CHFCl)_2 + S .$$

A number of free-radical reactions involving the addition of perhalogenoalkanes to vinyl fluoride have been investigated. Haszeldine et al.[112] irradiated trifluoroiodomethane and vinyl fluoride with ultraviolet light for 14 days and obtained an 84% yield of 1,1,1,3-tetrafluoro-3-iodopropane as well as a small amount of 1,1,1,3,5-pentafluoro-5-iodopentane:

$$CF_3I + H_2C{=}CHF \xrightarrow{h\nu} F_3C{-}CH_2{-}CHFI + F_3C{-}CH_2{-}CHF{-}CH_2{-}CHFI .$$

The addition of dibromodifluoromethane[113] and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane[114] to vinyl fluoride in an autoclave at 100°C in the presence of benzoyl peroxide has been described:

$$CBr_2F_2 + H_2C{=}CHF \rightarrow BrCF_2{-}CH_2{-}CHFBr + BrCF_2{-}CH_2{-}CHF{-}CH_2{-}CHFBr ,$$
$$BrCF_2{-}CBrFCl + H_2C{=}CHF \rightarrow BrCF_2{-}CFCl{-}CH_2{-}CHFBr + BrCF_2{-}CFCl{-}CH_2{-}$$
$$-CHF{-}CH_2{-}CHFBr .$$

Park et al.[115] showed that the free-radical addition of perfluorovinyl iodide to vinyl fluoride leads to the formation of 1,1,2,4-tetrafluoro-4-iodobut-1-ene:

$$H_2C{=}CHF + F_2C{=}CFI \rightarrow F_2C{=}CF{-}CH_2{-}CHFI .$$

The addition of trichloromethyl[116,117] and trifluoromethyl[118,119] radicals to vinyl fluoride has been reported. The free-radical addition of perfluoroacetonitrile to vinyl fluoride has been investigated[120]:

$$H_2C{=}CHF + F_2C{-}CN \rightarrow F_2C{-}CH_2{-}CHF{-}CN .$$

It has been shown[121] that the reaction of trichloro-, methyldichloro-, and trimethyl-silane with vinyl fluoride gives a high yield of the corresponding 2-fluoroethylsilanes:

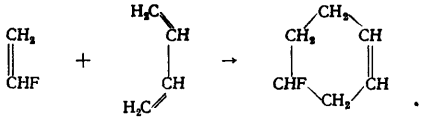
$$SiHCl_3 + H_2C{=}CHF \rightarrow CH_2F{-}CH_2{-}SiCl_3 .$$

The kinetics of the radical addition of tetrafluorohydrazine to vinyl fluoride have been studied[122]. It has been noted that the interaction of vinyl fluoride and ClF_3 in the gas phase at 70–125°C results, apart from substitution, in the addition of the decomposition products of chlorine trifluoride (Cl_2, F_2, ClF) to the double bond[123].

Haszeldine et al.[124] attempted to carry out the reaction of trifluoronitrosomethane with vinyl fluoride, but only the starting materials and the conversion products of trifluoronitrosomethane were isolated.

When tetramethyldiborane was allowed to react with vinyl fluoride, a mixture of ethyldimethyl-, diethylmethyl-, trimethyl-, fluorodimethyl-, and difluoromethyl-borane was obtained[125]. By allowing diborane to react with vinyl fluoride, Bartocha et al.[126] obtained a mixture of triethyl-, diethylfluoro-, and ethyldifluoro-borane with the last compound predominating; under these conditions, polymerisation of vinyl fluoride was not observed.

McQueen[127] showed that the reaction of vinyl fluoride with butadiene at 150–300°C and an elevated pressure, in the absence of polymerisation catalysts, gives a low yield of 4-fluorocyclohexene:



Soborovskii and coworkers[128,129] carried out the reaction of phosphorus trichloride with vinyl fluoride and obtained low yields of the chlorides of the isomeric 1-chloro-2-fluoro- and 2-chloro-2-fluoro-ethylphosphonic acids:

$$H_2C{=}CHF + 2PCl_3 + O_2 \rightarrow \begin{matrix} ClCH_2{-}CHF{-}P(O)Cl_2 \\ ClCHF{-}CH_2{-}P(O)Cl_2 \end{matrix}$$

Recently Jones[130] reported that butadiene is formed in high yield when vinyl fluoride is treated with tetraethylammonium trichlorostannate(II) in the presence of $PtCl_2$ and CsF in dimethylformamide, acetonitrile, or dimethyl sulphoxide:

$$CH_2{=}CHF + (C_2H_5)_4NSnCl_3 \xrightarrow[25°]{PtCl_2,CsF} H_2C{=}CH{-}CH{=}CH_2$$

Monofluorocyclopropane and its isomerisation products were obtained by the photolysis of keten in the presence of vinyl fluoride[131].

VI. POLYMERISATION OF VINYL FLUORIDE

The polymerisation of vinyl fluoride was observed for the first time by Starkweather in 1934[132]. Toluene was saturated with the monomer at −35°C, the solution was kept at 67°C and 6000 atm for 16 h, and the polymer was obtained in a low yield. Later, Newkirk[11] described the polymerisation of vinyl fluoride under ultraviolet irradiation in quartz capillaries in the presence of benzoyl, lauroyl, or acetyl peroxides as initiators.

Various methods have been described for the polymerisation of vinyl fluoride: emulsion, solution, suspension, and solid state. Emulsion polymerisation has found the widest application, since it takes place at a high rate at a relatively low temperature, which makes it possible to obtain a polymer with a high average molecular weight. Oxygen-free water or a mixture of water and organic solvents have been used as dispersion media[133–136].

Kalb et al.[39] studied the effect of impurities on the polymerisation of vinyl fluoride and found that, when the process is initiated with 0.2% of benzoyl peroxide at a pressure of 900 atm and a temperature of 80–100°C, 0.05% of oxygen in the monomer inhibits the polymerisation and 0.013% promotes it. Acetylene strongly inhibits the process, a brittle polymer of low molecular weight being formed in a yield of only 3%.

To improve the stability of the emulsions, emulsifying agents such as magnesium lauryl sulphate[137] or sodium bis(tridecyl)sulphosuccinate[138] are added to the system.

Redox systems, alkali metals, and substances which give rise to free radicals on heating have been investigated as initiators. Substances of the last type yielded polymers

with the most successful combination of properties [39,139]. Of the peroxy-catalysts, benzoyl [39,136,140-142], dodecanoyl [134], diethyl, di-t-butyl [39] peroxides and t-butyl hydroperoxide [138] have been tested for the polymerisation of vinyl fluoride. When dialkyl percarbonates are used as initiators, the polymerisation takes place at a lower temperature and pressure [143]. Apart from peroxides, azo-compounds have been widely used as initiators: $\alpha\alpha'$-azo-bis-$\alpha\gamma$-dimethylvaleronitrile, $\alpha\alpha'$-azobisisobutyronitrile [39,144], the hydrochloride of $\alpha\alpha'$-azobisisobutyramidine [39,145], azodisulphonates of alkali and alkaline earth metals [133], and the dihydrochloride of 2,2'-diamidino-2,2'-azopropane [146-149].

Tri-isobutylborane [134] and the products of the interaction of triethylborane with ammonia, hydrazine, hydroxylamine, and amines [150,151] have also been used for the polymerisation of vinyl fluoride.

The effect of various initiators on the polymerisation process has been studied [39]. Differences have been noted between initiators active at 125°C and above and those which activate polymerisation at 70–85°C. It was found that the polymers obtained at a high temperature had a lower molecular weight and more highly branched chains. The concentration of the initiator also affected the molecular weight of the polymer. With increase of the concentration of benzoyl peroxide in an aqueous medium at 80–90°C and a pressure of 250 atm, the effectiveness of the initiator and the characteristic viscosity of the polymer decreased. Analogous results were obtained when azo-compounds were employed as initiators.

The effect of temperature and pressure on the radical polymerisation of vinyl fluoride has been investigated. It has been established that, with increase of temperature, the effectiveness of the initiator reaches a maximum and then falls, the temperature corresponding to the maximum effectiveness being independent of pressure. As the reaction temperature rises, the viscosity of the poly(vinyl fluoride) (PVF) melt diminishes; an increase of pressure favours the formation of a polymer with a higher molecular weight [39].

Recently a number of continuous polymerisation processes have been developed for vinyl fluoride. Their essential feature consists of a continuous supply of vinyl fluoride, water, and the initiator into the reaction zone. The reaction is carried out in a homogeneous dispersion medium, the PVF formed being continuously removed. The required pressure and temperature are maintained in the reactor [145,146,149]. Processes with recycling of water, in which after the separation of the polymer water is deionised, freed from oxygen, and returned to the cycle, have been proposed [147-149].

In studies on the suspension polymerisation of vinyl fluoride much attention has been devoted to the search for new improved surface-active substances and stabilisers. Methylcellulose [137,152,153], glucose ethers [154], and the copolymers of ethylene [155], vinyl acetate, and allyl alcohol [156] with maleic acid or its anhydride have been suggested as dispersing agents for polymerisation in suspension. Using such compounds, it was possible to obtain highly porous PVF, which readily blends with plasticising agents, exhibits improved stability under illumination, and is a good electrical insulator. When lauroyl peroxide was used as an initiator, a polymer with a particle size of 0.05–2.5 μm was obtained [137]. The polymerisation of vinyl fluoride in the presence of titanium dioxide, yielding a product with a particle size of 0.3 μm, has been described [153].

PVF containing 14.4% of titanium dioxide and consisting largely of particles about 1 μm in diameter has been used in the form of dispersions in dimethylacetamide for coatings on metals.

In polymerisation in solution it is easier to control the reaction temperature, but, because of the lower concentration of the monomer, the polymers produced have a lower molecular weight. A number of organic solvents have been investigated as reaction media, using various polymerisation initiators: benzoyl, acetyl, lauroyl, diethyl, di-t-butyl [39,157,158], and perfluoroacyl [159-161] peroxides.

The search for new catalytic systems suitable for the polymerisation of vinyl fluoride has been vigorously prosecuted in recent years. The following systems have been tested: diethylaluminium bromide or triethyl aluminium–titanium tetrachloride [162,163], tri-isopropylaluminium–tetraisopropyloxytitanium [164], and cadmium and zinc alkyls [142]. Alkyl compounds of boron [165-168] and their coordination compounds with ammonia, hydrazine, hydroxylamine, and amines [150,151,169] have also been used as catalysts, which yielded PVF with a degree of crystallinity in excess of 30%. The polymerisation was carried out in solution, using methylene chloride, ethyl acetate, tetrahydrofuran, isobutyl alcohol, dimethylformamide, dimethyl sulphoxide, etc. as solvents [150]. A continuous process for the polymerisation of vinyl fluoride in carbon tetrachloride using peroxide initiators has been proposed [170]. It has been shown [39] that a common property of organic solvents is a tendency towards interaction (telomerisation) with vinyl fluoride, which leads to a sharp decrease of the molecular weight of the polymer obtained. Films produced from these polymers had a low impact strength.

Recently there has been a continuous increase in the number of experimental studies involving the use of radiation for the polymerisation of vinyl fluoride [171-177].

The use of radiation makes it possible to achieve polymerisation at low temperatures. Vinyl fluoride has been polymerised at a radiation dose rate ranging from 1×10^2 to 1×10^8 r h^{-1}. [73] The yield of PVF varied with the radiation dose and temperature, the maximum yield of the polymer being obtained at 0°C and a radiation dose rate of 10^4 r h^{-1}. [75] The polymerisation of vinyl fluoride at −78°C under γ-irradiation in the presence and absence of benzoyl peroxide has been studied [176].

VII. PROPERTIES OF POLY(VINYL FLUORIDE)

1. Physical Properties and Structure

A change in polymerisation conditions is reflected in the viscosity of the solutions and in the molecular weight of the resulting polymer. It has been shown [39] that the molecular weight is independent of the solvent used in the measurements. When benzoyl peroxide was employed, a decrease of the molecular weight of the polymer with increasing reaction temperature was observed. The molecular weight distribution of the polymer varies within wide limits as a function of the method of preparation, catalyst, and polymerisation temperature. Polymers synthesised using benzoyl peroxide as an initiator in the absence of a telogen melt at about 198°C.

Sapper [178] determined the heat of fusion per crystallising polymer unit, which amounted to 1800 cal.

The crystal structure of PVF has been studied by X-ray diffraction [167,179,180]. The NMR spectra of PVF have been recorded [181-183]. α-Particle absorption by PVF has been studied [184] at temperatures ranging from −59.7° to 42.7°C.

Ellison and Zisman[185] showed that the surface of PVF is readily wetted by solvents capable of forming hydrogen bonds.

2. Chemical Properties

Poly(vinyl fluoride) is resistant to the action of high temperatures, light, chemical reagents, and in particular hydrolysing agents. Characteristics such as tensile strength and modulus of elasticity do not change appreciably after exposure of the polymer to steam for 1500 h. After PVF specimens have been treated with 10% solutions of sodium hydroxide and hydrochloric acid for 7 days at 60°C, no changes in their mechanical properties were observed[186]. The treatment of PVF with nitrogen trifluoride and N_2F_2 at 80–100°C leads to formation of cross-links in the polymer and an improvement of its properties[187,188]. In the manufacture of laminate plastics adhesion between the carrier and the activated PVF layer can be achieved by the formation of OH, COOH, NH_2, etc. groups by treatment with boron trifluoride[189-191], concentrated sulphuric acid, hot alkali, or aluminium chloride[189].

Thermal decomposition of PVF in a vacuum at temperatures between 370°C and 500°C leads to the formation of hydrogen fluoride and fragments with different carbon chain lengths[192].

The telomerisation of vinyl fluoride by chloroformates at different temperatures in the presence of peroxides[193] and by trifluoromethyl iodide[194] has been investigated. The telomers obtained may be used as plasticisers for PVF. Telomers of chloroperfluoro-olefins and carbon tetrachloride have been recommended for the same purpose. Such plasticisers are not "sweated out" and do not cause turbidity of the specimen on bending[195]. Haszeldine et al.[196] carried out the telomerisation of vinyl fluoride with perhalogenoethanes under ultraviolet or X-ray irradiation or in the presence of peroxides at temperatures in the range 20–150°C.

The resistance of fluorine-containing polymers to ionising radiation has been investigated[197]. It has been found that polytetrafluoroethylene retains its structural properties only up to a dose rate of 2 Mrad, while PVF is stable up to 32 Mrad. After irradiation and simultaneous heat treatment the polymers become brittle.

Bro[198] studied the stability of various polymers in relation to amines and found that the PVF film is stable under the action of n-butylamine.

3. Stabilisation

Although PVF is distinguished by a comparatively high resistance to oxidative thermal and light-induced degradation, a number of stabilisers have been proposed for the preparation of compositions based on it which would be stable in various applications and under different processing conditions.

Monoalkyl esters of fumaric and maleic acids[199], glyceryl monolaurate[200], substituted 6-methyleneoctahydronaphthalenes[201], unsaturated terpenes and disulphides[202], alkali metal formates[203], and the copolymer of vinyl fluoride with bicyclo[2,2,1]hept-2-ene[204] have been proposed as thermostabilisers for PVF.

Benzophenone[205], *O*-hydroxybenzophenone[206], 2,2′-dihydroxy-4,4′-dimethoxybenzophenone[207,208], 2,2′,4,4′-tetrahydroxybenzophenone[209], substituted triazoles[210], poly(2-hydroxy-4-methacryloyloxybenzophenone)[211], and a polyester obtained from the dichloride of adipic acid and 2,4,4′-trihydroxybenzophenone[212] proved to be effective photostabilisers under the action of ultraviolet light.

4. Processing and Applications

PVF is processed by the usual methods for thermoplastic materials: by extrusion, by pressing, by casting under pressure at temperatures in excess of 200°C, and also by deposition of coatings from dispersions[39,203,207-211,213-215].

PVF has found wide application in the form of films. Films are most often formed from solutions[39] or dispersions containing various substances which function as latent solvents for PVF[213,215-220]. Dimethylformamide[39], various lactones, for example γ-butyrolactone[213,217,219], tetramethylurea, dimethylacetamide, triethyl phosphate[216], 2-pyrrolidinone, *N*-isopropyl-*N*-methyl-, and 5-methyl-2-pyrrolidinone[218], *N*-formyl- and *N*-acetyl-piperidine[220], and dimethyl sulphoxide[214,215] have been used as solvents. A method has been described for the preparation of electroluminescent films from dispersions containing zinc sulphide[221]. To prepare opaque PVF films and dispersions, 1–35% of titanium dioxide, calcium carbonate, or their mixtures have been added. Pigments, stabilisers, and plasticisers have also been introduced into the films[222-227]. A method has been described[228] for the preparations of transparent films with low reflectivity by adding to PVF 1–5% of silica in the form of homogeneous spherical particles 2–10 μm in diameter. PVF films have been used in the manufacture of laminate plastics with high stability to wear and the effect of light[229-232].

Simril and Curry[186] made a detailed study of the physical, chemical, optical, and electrical properties of PVF films, and also of the effect of diaxial orientation of the films on some of their physical properties. PVF is transparent to visible and ultraviolet light but absorbs strongly in the infrared. PVF films have high tensile, bending, and impact strength, exhibit high resistance to wear, and undergo high relative elongation on stretching.

The principal distinctive feature of PVF is its high resistance to weathering. After exposure to sunlight for 7 years, a PVF film retained 50% of its initial tensile strength and remained flexible[39,233,234]. The permeability of PVF films to water and also to water vapour and various organic compounds and gases has been investigated[234-236]. A relation between the degree of orientation of the films and some of their mechanical properties has been demonstrated[39,237,238]. A highly oriented film shows a higher, tensile, impact, and bending strength and also exhibits a higher tear resistance.

To improve its adhesion to various materials, the film has been treated in a flame for periods ranging from 0.0025 to 0.5 s, with solutions of alkali metals in liquid ammonia, with organic derivatives of aluminium, zinc, and magnesium, and also with a solution of a diazo-compound in toluene, for example ethyl diazoacetate, 4,4′-bis-(dimethylaminophenyl)diazomethane, etc. with subsequent irradiation of the treated surface by ultraviolet light[239-244].

The preparation of filaments from a dispersed paste containing 20–70% PVF has been described[245]. PVF in the form of films oriented to different extents has found a wide variety of applications in electrical insulation, packing, in the glazing of forcing frames, and in the protection of horticultural crops. Its exceptionally high resistance to the action of ultraviolet radiation makes PVF a very promising material for the protection of surfaces in apparatus designed for the collection of solar energy[246], in the

building industry[233,247,248], and for protective coatings on metals[249-254]. The applications of PVF for internal coatings[255], for the preparation of diaphragms in electrolysers for the manufacture of chlorine[256], and also in chemical engineering[257] have been described.

VIII. COPOLYMERS OF VINYL FLUORIDE

Much work has been devoted[258-299] to the preparation, investigation of the properties, and applications of the copolymers of vinyl fluoride with various unsaturated compounds. The methods for the synthesis of vinyl fluoride copolymers are completely analogous to those for the synthesis of PVF. The copolymerisation has been carried out in suspension[155,156,164,268], in emulsion[138,150,152,261,263-265,272,288], in solution[166,167,170,259,262,263,266,288,295,296,299], or in the solid state[150,268,278,288,289]. A list of binary copolymers (comonomers) is given in Table 2.

Table 2. Binary copolymers of vinyl fluoride

Comonomer	References	Comonomer	References
Ethylene	138,150,262,277,279,299	Vinyl butyrate	156,274
Tetrafluoroethylene	142,150,167,168,263, 266,279,299	Propene	278,290
Vinyl acetate	159,260,269,270,274, 289, 297	Isobutene	152
Vinylidene fluoride	142,167,170,265,274,299	Bicycloheptene	138
Trifluoroethylene	170,268	Diethyl maleate	155,156
Vinyl chloride	150,164,166,168,271,275, 276,280,283,289,299	Acrylate and methacrylate esters	159,299
Methylenemalononitrile	267	Vinyl benzoate	156
α-Acetamidoacrylamide	258	Dioctyl fumarate	156
Hydrogen cyanide	259	Vinyl carbonate	284
Chlorotrifluoroethylene	170,261,271,299	Acrylonitrile	156,296,299
Dichlorodifluoroethylene	264	Perfluoropropene	150,285,299
α-Cyanoacrylamide	267	Acrylamide	156
Methylenemalonamide	267	1,1,2,4-Tetrafluorobuta-1,3-diene	286
Fluoromethacrylate esters	273	1,1,2- and 1,1,3-trifluorobutadiene	287
Vinylidene chloride	299	1,1-Difluoroisobutene	288
Vinyl propionate	274,289	Perfluoronitrosomethane	291
		Styrene	299

The copolymers of vinyl fluoride are processed by the same methods as those used for PVF. The copolymers are widely used in the form of films[139,150,260,263,270,279,287,288] and coatings[271,286,287,298]. Coatings made from the copolymer of vinyl fluoride and vinyl chloride make various rubber articles resistant to light. Specimens with such coating remained unchanged after irradiation for 20 h with ultraviolet light, while ordinary rubber withstood only 7.5–25 min of such treatment[282]. The synthesis of foam plastics based on a copolymer of vinyl fluoride and vinyl chloride has been described.

Dimethyl sulphoxide, furfural, tetrahydrofuran, and dichlorobenzene have been used as solvents in the manufacture of fibre from the copolymers of vinyl fluoride and vinyl chloride; the fibre was spun by a wet method[150,270,280]. Copolymers of vinyl fluoride with isobutene and perfluoropropene proved to be resistant to heat, light, and chemical reagents. Extruded sheets of such copolymers are strong, flexible, and transparent, and, by virtue of their capacity for cold draining, can be used for the manufacture of various articles[150,152,155].

The synthesis of ternary copolymers has also been described. Thus the copolymer of vinyl fluoride, tetrafluoroethylene, and chlorotrifluoroethylene has been obtained in aqueous suspension at 80°C in the presence of benzoyl peroxide[292]. The copolymer of vinyl fluoride, tetrafluoroethylene, and vinyl chloride is incombustible and is readily soluble in acetone, ethyl methyl ketone, ethyl acetate, and halogeno-derivatives of hydrocarbons[293]. Copolymers melting without decomposition have been obtained from vinyl fluoride, dialkyl maleates, and vinylidene halides[294]. The copolymerisation of vinylidene fluoride, vinyl fluoride, and chlorotrifluoroethylene on γ-irradiation of the monomers has been described[274].

REFERENCES

1. I. L. Knunyants and A. V. Fokin, Uspekhi Khim., 20, 419 (1951).
2. P. Vaculik, "Chemie Monomeru" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 250.
3. F. Swarts, Bull. Acad. roy Belg., 383 (1901).
4. F. Swarts, Bull. Acad. roy Belg., 728 (1909).
5. F. Swarts, Bull. Soc. chim. France [4], 25, 145 (1919).
6. A. V. Grosse and C. B. Linn, J. Amer. Chem. Soc., 64, 2289 (1942).
7. BRD P. 362 750 (1922); Friedl., 14, 110 (1926).
8. J. Söll, BRD P. 641 878 (1937); Chem. Abs., 31, 5809 (1937).
9. J. C. Hillyer, US P. 2 480 021 (1949); Chem. Abs., 44, 1127 (1950).
10. V. Reinoehl, Czech P. 103 135 (1962); Chem. Abs., 59, 1135 (1963).
11. A. E. Newkirk, J. Amer. Chem. Soc., 68, 2467 (1946).
12. I. M. Dolgopol'skii, K. Vaistariene, and J. Krauciunas, Trudy Akad. Nauk Lit. SSR, Ser. B-3, 95 (1965).
13. B. P. 600 296 (1948); Chem. Abs., 42, 7312 (1948).
14. B. P. 580 910 (1946); Chem. Abs., 41, 2428 (1947).
15. L. F. Salisbury, US P. 2 519 199 (1950); Chem. Abs., 45, 2496 (1951).
16. L. F. Salisbury, US P. 2 469 848 (1949); Chem. Abs., 43, 7035 (1949).
17. R. Petit, C. Kaziz, and G. Wetroff, French P. 1 324 408 (1963); Chem. Abs., 59, 11 247 (1963).
18. A. Bluemcke, P. Fischer, and W. Krings, BRD P. 1 259 329 (1968); Chem. Abs., 68, 68 452 (1968).
19. G. M. Whitman, US P. 2 401 850 (1946); Chem. Abs., 40, 6091 (1946).
20. B. P. 603 855 (1948); Chem. Abs., 43, 660 (1949).
21. Belg. P. 612 914 (1962); Chem. Abs., 58, 1344 (1963).
22. P. J. Manno and W. H. Snaveley, BRD P. 1 210 799 (1966); Chem. Abs., 64, 15 740 (1966).
23. J. C. Hillyer and J. F. Wilson, US P. 2 471 525 (1949); Chem. Abs., 43, 6645 (1949).
24. J. C. Hillyer and J. F. Wilson, US P. 2 634 300 (1953); Chem. Abs., 48, 2082 (1954).
25. R. Petit, C. Kazis, and G. Wetroff, BRD P. 1 325 750 (1963); Chem. Abs., 59, 11 248 (1963).
26. French P. 1 383 927 (1965); Chem. Abs., 62, 11686 (1965).
27. F. J. Christoph, US P. 3 395 187 (1968); Chem. Abs., 69, 66 893 (1968).
28. J. W. Begley and R. M. Marsheck, US P. 3 397 247 (1968); Chem. Abs., 69, 76 605 (1968).
29. B. F. Skiles, US P. 2 716 143 (1955); Chem. Abs., 50, 7840 (1956).
30. J. C. Hillyer and J. F. Wilson, US P. 2 574 480 (1951); Chem. Abs., 46, 4026 (1952).
31. B. F. Skiles, US P. 2 716 142 (1955); Chem. Abs., 50, 7840 (1956).

32. B. F. Skiles, US P. 2 892 000 (1959); Chem. Abs., 54, 1296 (1960).
33. J. W. Clark, US P. 2 626 963 (1953); Chem. Abs., 48, 1407 (1954).
34. J. D. Calfee and F. H. Bratton, US P. 2 462 359 (1949); Chem. Abs., 43, 3834 (1949).
35. C. B. Linn, US P. 2 762 849 (1956); Chem. Abs., 51, 10 556 (1957).
36. L. Foulletier, French P. 1 410 317 (1965); Chem. Abs., 64, 589 (1966).
37. Kato Kaoru, Wada Hiroyuki, and Kawakami Yasumasa, Japanese P. 6807, 202 (1968); Chem. Abs., 69, 58 822 (1968).
38. W. A. McMillan, J. Amer. Chem. Soc., 58, 1345 (1936).
39. G. H. Kalb, D. D. Coffman, T. A. Ford, and F. L. Johnston, J. Appl. Polymer Sci., 4, No. 10, 55 (1960).
40. Belg. P. 626 014 (1963); Chem. Abs., 59, 9789 (1963).
41. K. H. Mieglitz, H. Heinze, and H. Linke, BRD P. 1 191 804 (1965); Chem. Abs., 63, 6859 (1965).
42. K. Vaistariene and J. Krauciunas, Trudy Akad. Nauk Lit. SSR, Ser. B-3, 103 (1965).
43. K. Mieglitz, BRD P. 1 134 664 (1962); Chem. Abs., 58, 3314 (1963).
44. Kh. U. Usmanov, A. A. Yul'chibaev, and G. S. Dorzhin, Zhur. Prikl. Khim., 41, 218 (1968).
45. French P. 805 563 (1936); Chem. Zentr., I, 2258 (1937).
46. J. Harmon, Canad. P. 491 856 (1963).
47. D. Sianesi, G. Nelli, and R. Fontanelli, Chim. e Ind., 619 (1968).
48. O. W. Cass, US P. 2 442 993 (1948); Chem. Abs., 42, 6839 (1948).
49. B. P. 619 394 (1949); Chem. Abs., 43, 6645 (1949).
50. D. D. Coffman and R. D. Cramer, US P. 2 461 523 (1949); Chem. Abs., 43, 3437 (1949).
51. B. F. Skiles, US P. 2 674 632 (1954); Chem. Abs., 49, 4007 (1955).
52. T. B. Downing, A. F. Benning, and R. C. McHarness, US P. 2 480 560 (1949); Chem. Abs., 44, 4922 (1950).
53. F. Harmon, US P. 2 599 631 (1952); Chem. Abs., 47, 1725 (1953).
54. A. E. Pavlath and F. H. Walker, US P. 3 118 005 (1964); Chem. Abs., 60, 14 385 (1964).
55. Dutch P. 6 405 140 (1964); Chem. Abs., 62, 10 334 (1965).
56. A. L. Henne and T. Midgley, J. Amer. Chem. Soc., 58, 882 (1936).
57. A. L. Henne, J. Amer. Chem. Soc., 60, 2275 (1938).
58. A. F. Benning, F. D. Downing, and P. J. Plunkett, US P. 2 401 897 (1946); Chem. Abs., 40, 5066 (1946).
59. C. L. Thomas, US P. 2 673 884 (1954); Chem. Abs., 49, 4007 (1955).
60. D. Sianesi and G. Nelli, Belg. P. 633 525 (1963); Chem. Abs., 61, 1755 (1964).
61. M. Otto, H. Theobald, and R. Melon, BRD P. 859 887 (1952); Chem. Abs., 47, 11 219 (1953).
62. French P. 1 399 051 (1965); Chem. Abs., 63, 5529 (1965).
63. H. W. Daut and M. A. Youker, US P. 2 005 710 (1935); Chem. Zentr. I, 501 (1936).
64. French P. 43 972 (1934); Chem. Zentr. I, 2255 (1935).
65. R. M. Hedrick, US P. 2 695 320 (1954); Chem. Abs., 50, 2652 (1956).
66. G. M. Whitman, US P. 2 578 913 (1951); Chem. Abs., 46, 6138 (1952).
67. F. Nerdel, Naturwiss., 39, 209 (1952).
68. R. E. Robinson, US P. 3 379 780 (1968); Chem. Abs., 69, 51 530 (1968).
69. J. C. Crano, E. K. Fleming, and G. M. Trenta, J. Amer. Chem. Soc., 90, 5036 (1968).
70. R. D. Cramer and F. N. Jones, US P. 3 356 748 (1967); Chem. Abs., 68, 29 239 (1968).
71. J. P. Henry, C. E. Rectenwald, and J. W. Clark, BRD P. 1 175 225 (1964); Chem. Abs., 63, 2897 (1965).
72. S. D. Rosenberg, B. P. 826 619 (1960); Chem. Abs., 54, 15 218 (1960).
73. B. P. 1 020 716 (1966); Chem. Abs., 64, 15 740 (1966).
74. Masuhiko Tamura and Teruo Yasui, Japanese P. 9525 (1968); Ref. Zhur. Khim., 10N29 (1969).
75. G. O. Pritchard, M. Venugopalan, and T. F. Graham, J. Phys. Chem., 68, 1786 (1964).
76. J. Copecny, N. Lucanska, F. Spirka, E. Cerny, and D. Ambroz, Pracovni Lekar., 16, 301 (1964).
77. P. G. Maslov and Yu. P. Maslov, Khim. i Tekh. Topliv i Masel, 3, No. 10, 50 (1958).
78. A. M. Mirri, A. Guarnieri, and P. Favero, Nuovo cimento, 19, 1189 (1961).
79. G. Favini, Gazzetta, 92, 244 (1962).
80. J. Momigny, Nature, 199, 1179 (1963).
81. C. Lifshitz and F. A. Long, J. Phys. Chem., 67, 2463 (1963).
82. R. Bralsford, P. V. Harris, and W. C. Price, Proc. Roy. Soc., A 258, 459 (1960).
83. B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, Spectrochim. Acta, 13, 120 (1958).
84. H. W. Morgan and J. H. Goldstein, J. Phys. Chem., 30, 1025 (1959).
85. D. R. Lide and D. Christensen, Spectrochim. Acta, 17, 665 (1961).
86. K. S. Pitzer and N. K. Freeman, J. Chem. Phys., 14, 586 (1946).
87. A. R. H. Cole and H. W. Thompson, Proc. Roy. Soc., A, 200, 10 (1949).
88. P. Torkington, Chem. Phys., 17, 1279 (1949).
89. P. Torkington, Proc. Roy. Soc., A, 206, 17 (1951).
90. H. J. Bernstein, Canad. J. Chem., 34, 617 (1956).
91. L. M. Sverdlov, Yu. V. Klochkovskii, V. S. Kukina, and T. D. Mezhueva, Optika i Spektrosk., 9, 728 (1960).
92. P. Torkington and H. W. Thompson, Trans. Faraday Soc., 41, 236 (1945).
93. B. Bak and D. Christensen, Spectrochim. Acta, 12, 355 (1958).
94. B. Bak and D. Christensen, Acta Chem. Scand., 12, 1147 (1958).
95. J. R. Scherer and W. J. Potts, J. Chem. Phys., 31, 1691 (1959).
96. C. N. Banwell, N. Sheppard, and J. J. Turner, Spectrochim. Acta, 16, 794 (1960).
97. C. N. Banwell and N. Sheppard, Mol. Phys., 3, 351 (1960).
98. C. N. Banwell and N. Sheppard, Proc. Roy. Soc., A, 263, 136 (1961).
99. W. Brügel, T. Ankel, and F. Krückeberg, Z. Elektrochem., 64, 1121 (1960).
100. G. S. Reddy and J. H. Goldstein, J. Chem. Phys., 35, 380 (1961).
101. R. F. Mayo and J. H. Goldstein, J. Mol. Spectroscopy, 14, 173 (1964).
102. H. S. Gutowsky, M. Karplus, and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).
103. C. N. Banwell, A. D. Cohen, N. Sheppard, and J. J. Turner, Proc. Chem. Soc., 266 (1959).
104. P. G. T. Fogg and J. D. Lambert, Proc. Roy. Soc., A, 232, 537 (1955).

105. V.G. Martur, S.A. Antipova, and V.S. Kozlova, Ukrain. Khim. Zhur., 32, 391 (1966).
106. H.T. Rein, M.E. Miville, and A.H. Fainberg, Analyt. Chem., 35, 1536 (1963).
107. P.J. Abell, Trans. Faraday Soc., 60, 2214 (1964).
108. A. Ya. Yakubovich, V.A. Shpanskii, and A.L. Lemke, Zhur. Obshch. Khim., 24, 2257 (1954).
109. A. Ya. Yakubovich, V.A. Shpanskii, and A.L. Lemke, Dokl. Akad. Nauk SSSR, 96, 773 (1954).
110. E.K. Ellingboe, US P. 2 439 203 (1948); Chem. Abs., 42, 5046 (1948).
111. N.N. Yarovenko and A.S. Vasil'eva, Zhur. Obshch. Khim., 31, 3021 (1961).
112. R.N. Haszeldine and B.R. Steele, J. Chem. Soc., 1199 (1953).
113. P. Tarrant and M.R. Lilyguist, J. Amer. Chem. Soc., 77, 2783 (1955).
114. P. Tarrant and M.R. Lilyguist, J. Amer. Chem. Soc., 77, 3640 (1955).
115. J.D. Park, R.J. Seffl, and J.R. Lacher, J. Amer. Chem. Soc., 78, 59 (1956).
116. J.M. Tedder and J.C. Walton, Trans. Faraday Soc., 62, 1859 (1966).
117. J.M. Tedder and J.C. Walton, Proc. Chem. Soc., 420 (1964).
118. P.S. Dixon and M. Szwarc, Trans. Faraday Soc., 59, 112 (1963).
119. J.M. Pearson and M. Szwarc, Trans. Faraday Soc., 60, 553 (1964).
120. G.J. Janz and J.B. Flannery, J. Phys. Chem., 70, 2061 (1966).
121. D. Cooper, R.N. Haszeldine, and M.J. Newlands, J. Chem. Soc., (A), 2098 (1967).
122. A.J. Dijkestra, J.A. Kerr, and A.F. Trotman-Dickenson, J. Chem. Soc., (A), 864 (1967).
123. B. Cornils, G. Stoeckelmann, and G. Schiemann, J. prakt. Chem., 35, 205 (1967).
124. R.E. Banks, R.N. Haszeldine, H. Sutcliffe, and C.J. Willis, J. Chem. Soc., 2506 (1965).
125. J.M. Birchall, R.N. Haszeldine, and J.F. Marsh, Chem. Ind., 1080 (1961).
126. B. Bartocha, W.A.G. Graham, and F.G.A. Stone, J. Inorg. Nucl. Chem., 6, 119 (1958).
127. D.M. McQueen, US P. 2 904 598 (1959).
128. L.Z. Soborovskii, Yu.M. Zinov'ev, and T.G. Spiridonova, Zhur. Obshch. Khim., 29, 1139 (1959).
129. Yu.M. Zinov'ev, T.G. Spiridonova, and L.Z. Soborovskii, Zhur. Obshch. Khim., 29, 3594 (1959).
130. F.N. Jones, J. Org. Chem., 32, 1667 (1967).
131. F. Casas, J.A. Cerr, and A.F. Trotman-Dickenson, J. Chem. Soc., 1141 (1965).
132. H.W. Starkweather, J. Amer. Chem. Soc., 56, 1870 (1934).
133. J.A. Robertson, US P. 2 468 111 (1949); Chem. Abs., 43, 5642 (1949).
134. J. Kresta, L. Ambroz, and J. Kratochvil, Chem. Prumysl., 16, 282 (1966).
135. J.L. Hecht and C.T. Hughes, French P. 1 445 328 (1966); Chem. Abs., 66, 56 010 (1967).
136. Dutch P. 6 607 093 (1966); Chem. Abs., 66, 86 116 (1967).
137. W.A. Gallup and J.R. Semancik, French P. 1 388 525 (1965); Chem. Abs., 63, 10 089 (1965).
138. R.D. Burkhart, N.L. Zütty, and R.D. Lundberg, Belg. P. 645 961 (1964); Chem. Abs., 63, 10 087 (1965).
139. D. Sianesi and G. Caporiccio, French P. 1 464 332 (1966); Chem. Abs., 67, 54 590 (1967).
140. D.D. Coffman and T.A. Ford, US P. 2 419 008 (1947); Chem. Abs., 41, 4963 (1947).
141. B.P. 1 057 088 (1967); Chem. Abs., 66, 66 041 (1967).
142. G. Caporiccio and E. Strepparola, Ital. P. 704 235 (1966); Chem. Abs., 68, 22 367 (1968).
143. French P. 1 419 741 (1965); Chem. Abs., 65, 9049 (1966).
144. F.L. Johnston and D.C. Pease, US P. 2 510 783 (1950); Chem. Abs., 46, 1299 (1952).
145. B.P. 905 879 (1962); Chem. Abs., 58, 5808 (1963).
146. J.L. Hecht, Belg. P. 617 777 (1962); Chem. Abs., 58, 6947 (1963).
147. V.E. James, Belg. P. 614 581 (1962); Chem. Abs., 58, 9253 (1963).
148. B.P. 940 176 (1963); Chem. Abs., 60, 6953 (1964).
149. Dutch P. 6 511 117 (1966); Chem. Abs., 65, 3994 (1966).
150. D. Sianesi, G. Caporiccio, and E. Strepparola, Belg. P. 635 081 (1963); Chem. Abs., 62, 663 (1965).
151. D. Sianesi, G. Caporiccio, and E. Strepparola, Belg. P. 646 722 (1964); Chem. Abs., 63, 8519 (1965).
152. W.A. Gallup, Belg. P. 645 617 (1964); Chem. Abs., 63, 8566 (1965).
153. Dutch P. 6 500 955 (1965); Chem. Abs., 64, 3725 (1966).
154. R.O.L. Lynn and H.W. Mohrman, US P. 2 862 913 (1958).
155. R.J. Longly and R.H. Martin, US P. 2 823 200 (1958).
156. R.I. Martin, US P. 2 917 494 (1959).
157. B.P. 607 499 (1948); Chem. Abs., 43, 3659 (1949).
158. A.E. Newkirk, US P. 2 479 957 (1949); Chem. Abs., 43, 9530 (1949).
159. D.M. Young and W.N. Stoops, US P. 2 792 423 (1957).
160. M.I. Bro, R.J. Convery, and R.C. Schreyer, B.P. 840 080 (1960); Chem. Abs., 55, 1071 (1961).
161. R.A. Darby and E.K. Ellingboe, US P. 3 069 404 (1962); Chem. Abs., 58, 5805 (1963).
162. G.H. Grawford, US P. 3 084 144 (1963); Chem. Abs., 59, 1780 (1963).
163. G.F. Helfrich and E.J. Rothermel, US P. 3 380 977 (1968); Chem. Abs., 68, 115 212 (1968).
164. D. Sianesi and G. Caporiccio, Belg.P. 618 320 (1962); Chem. Abs., 58, 9247 (1963).
165. E.J. Welch, US P. 3 112 298 (1963); Chem. Abs., 60, 5661 (1964).
166. Belg. P. 562 433 (1958); Chem. Abs., 53, 11 887 (1959).
167. G. Natta, G. Allegra, I.W. Bassi, and E. Forti, J. Polymer Sci., A3, 4263 (1965).
168. Ital. P. 704 906 (1966); Chem. Abs., 68, 22 370 (1968).
169. D. Sianesi, G. Caporiccio, and E. Strepparola, Belg. P. 646 722 (1964); Chem. Abs., 63, 8519 (1965).
170. E. Fischer and G. Bier, BRD P. 1 086 433 (1960); Chem. Abs., 55, 19 344 (1961).
171. Belg. P. 615 568 (1962); Chem. Abs., 57, 15 368 (1962).
172. P.J. Manno and W.H. Snavely, B.P. 919 683 (1963); Chem. Abs., 58, 14 146 (1963).
173. French P. 1 394 584 (1965); Chem. Abs., 63, 13 449 (1965).
174. P.J. Manno, Nucleonics, 22, 72 (1964).
175. P.J. Manno, Am. Chem. Soc. Div. Polymer Chem., 4, 79 (1963); Chem. Abs., 62, 697 (1965).
176. Kh.U. Usmanov, A.A. Yul'chibaev, and R. Mukhamedzhanov et al., Symposium, "Fizika i Khimiya

Prirodnykh i Sinteticheskikh Polimerov" (The Physics and Chemistry of Natural and Synthetic Polymers), Izd. Akad. Nauk Uzbek. SSR, Tashkent, 1962, No. I, p. 205.
177. E. V. Volkova, P. V. Zimakov, and A. V. Fokin, Dokl. Akad. Nauk SSSR, **167**, 1057 (1966).
178. D. I. Sapper, J. Polymer Sci., **43**, 383 (1960).
179. R. C. Golike, J. Polymer Sci., **42**, 583 (1960).
180. G. Natta, I. W. Bassi, and G. Allegra, Atti. Accad. naz. Lincei, Rend. Classe Sci. fis., mat. nat., **31**, 350 (1961).
181. W. P. Slichter, J. Polymer Sci., **24**, 173 (1957).
182. R. E. Naylor and S. W. Lasoski, J. Polymer Sci., **44**, 1 (1960).
183. F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, J. Chem. Phys., **39**, 1199 (1963).
184. Y. Ishida and K. Yamafuji, Kolloid. Z., **200**, 50 (1964).
185. A. H. Ellison and W. A. Zisman, J. Phys. Chem., **58**, 260 (1954).
186. V. L. Simril and B. A. Curry, J. Appl. Polymer Sci., **4**, No. 10, 62 (1960).
187. B. P. 895 619 (1962); Chem. Abs., **57**, 3635 (1962).
188. T. L. Cairns and C. S. Cleaver, US P. 3 162 623 (1964); Chem. Abs., **62**, 7942 (1965).
189. B. P. 834 196 (1960); Chem. Abs., **54**, 25 975 (1960).
190. Belg. P. 610 318 (1962); Chem. Abs., **57**, 11 398 (1962).
191. R. O. Osborn, US P. 3 122 445 (1964); Chem. Abs., **60**, 12 191 (1964).
192. S. L. Madorsky, W. E. Hart, S. Straus, and V. A. Sedlak, J. Res. Nat. Bur. Stand., **51**, 327 (1953).
193. W. S. Barnhart, US P. 2 817 678 (1957).
194. T. J. Dougherty, J. Amer. Chem. Soc., **86**, 460 (1964).
195. W. S. Barnhart, US P. 2 820 772 (1958); Chem. Abs., **52**, 6845 (1958).
196. R. N. Haszeldine, B. P. 869 364 (1961).
197. R. Timmerman and W. Greyson, J. Appl. Polymer Sci., **6**, 456 (1962).
198. M. I. Bro, J. Appl. Polymer Sci., **1**, 310 (1959).
199. J. R. Darby, US P. 2 457 035 (1948); Chem. Abs., **43**, 2037 (1949).
200. F. L. Johnson and H. J. Richter, US P. 2 476 606 (1949); Chem. Abs., **43**, 8740 (1949).
201. J. M. Quinn and A. K. Schneider, US P. 2 999 838 (1961); Chem. Abs., **55**, 27 968 (1961).
202. B. P. 898 182 (1962); Chem. Abs., **57**, 8743 (1962).
203. H. B. West, US P. 2 996 478 (1958); Chem. Abs., **56**, 596 (1962).
204. R. D. Lundberg and F. E. Bailey, US P. 3 294 767 (1966); Chem. Abs., **66**, 38 500 (1967).
205. H. H. Fanning, US P. 3 297 462 (1967); Chem. Abs., **66**, 66 388 (1967).
206. S. Tocker, US P. 3 288 880 (1966); Chem. Abs., **66**, 29 601 (1967).
207. D. I. Sapper, US P. 2 917 402 (1959); Chem. Abs., **54**, 8150 (1960).
208. B. P. 872 421 (1958); Chem. Abs., **56**, 3654 (1962).
209. D. E. Brasure, US P. 2 970 066 (1961); Chem. Abs., **55**, 12 925 (1961).
210. M. F. Bruno, US P. 3 018 269 (1962); Chem. Abs., **57**, 6147 (1962).
211. S. Tocker, Belg. P. 629 480 (1963); Chem. Abs., **61**, 8484 (1964).
212. S. Tocker, US P. 3 385 910 (1968); Chem. Abs., **69**, 20 060 (1968).
213. B. P. 837 839 (1960); Chem. Abs., **54**, 21 866 (1960).
214. B. P. 862 853 (1961); Chem. Abs., **55**, 17 098 (1961).
215. J. S. Proctor, US P. 3 096 299 (1963); Chem. Abs., **59**, 8949 (1963).
216. M. F. Bechtold and M. I. Bro, US P. 2 810 702 (1957); Chem. Abs., **52**, 19 252 (1958).
217. L. R. Barton, US P. 2 953 818 (1960); Chem. Abs., **55**, 4052 (1961).
218. L. R. Barton, US P. 3 000 843 (1959); Chem. Abs., **56**, 564 (1962).
219. M. I. Bro, US P. 3 000 844 (1959); Chem. Abs., **56**, 564 (1962).
220. J. S. Proctor, US P. 3 110 692 (1963); Chem. Abs., **60**, 4313 (1964).
221. D. T. Meloon and R. O. Osborn, US P. 2 976 446 (1961); Chem. Abs., **55**, 11 109 (1961).
222. Belg. P. 638 252 (1964); Chem. Abs., **62**, 10 637 (1965).
223. J. W. L. Fordham, French P. 1 388 580 (1965); Chem. Abs., **63**, 10 148 (1965).
224. Dutch P. 6 601 315 (1966); Chem. Abs., **65**, 9133 (1966).
225. J. L. Brennan, W. L. Bryan, and R. J. Kieffer, US P. 3 326 739 (1967); Chem. Abs., **68**, 22 794 (1968).
226. G. I. Deak and F. E. Izzo, US P. 3 364 049 (1963); Chem. Abs., **68**, 51 052 (1968).
227. P. S. Bettoli, US P. 3 300 927 (1967); Chem. Abs., **66**, 66 287 (1967).
228. Dutch P. 6 601 864 (1966); Chem. Abs., **65**, 12 378 (1966).
229. J. C. Bonacci and L. E. Wolinski, US P. 3 284 277 (1966); Chem. Abs., **66**, 19 382 (1967).
230. R. I. Elliot and F. R. Ashby, US P. 3 284 967 (1966); Chem. Abs., **66**, 66 962 (1967).
231. E. C. Hale and P. S. Kerekes, Canad. P. 786 303 (1968); Chem. Abs., **69**, 44 423 (1968).
232. P. R. Noyes, US P. 3 369 959 (1968); Chem. Abs., **68**, 69 870 (1968).
233. R. R. Irving, Iron Age, **188**, No. 7, 95 (1961).
234. N. L. Simril and B. A. Curry, Mod. Plast, **36**, No. 11, 121, 124, 168 (1959).
235. E. L. Davis, M. Karel, and B. E. Proctor, Mod. Packaging, **33**, No. 7, 208, 283 (1960).
236. J. Sivadjian and D. Riberio, J. Appl. Polymer Sci., **8**, 1403 (1964).
237. C. J. Heffelfinger, Belg. P. 625 357 (1963); Chem. Abs., **60**, 14 707 (1964).
238. R. S. Prengle and R. L. Richards, US P. 3 139 470 (1964); Chem. Abs., **61**, 7203 (1964).
239. B. P. 923 846 (1963); Chem. Abs., **58**, 14 257 (1963).
240. W. L. Bryan and D. E. Swarts, Belg. P. 635 086 (1964); Chem. Abs., **61**, 13 502 (1964).
241. W. L. Bryan and D. E. Swarts, Belg. P. 635 087 (1964); Chem. Abs., **61**, 13 502 (1964).
242. W. L. Bryan, Belg. P. 637 742 (1964); Chem. Abs., **62**, 6649 (1965).
243. M. Reiher, D. Schleede, and K. Weissermel, BRD P. 1 017 308 (1957); Chem. Abs., **54**, 11 581 (1960).
244. A. W. Morgan and J. S. Swenson, US P. 3 376 278 (1968); Chem. Abs., **68**, 105 746 (1968).
245. C. B. Satterthwaite, US P. 2 824 780 (1958); Chem. Abs., **52**, 8577 (1958).
246. J. Schweinichen, Materie Plast., **28**, 221 (1962).
247. O. Jonsson, Plastvärlden, **12**, 60 (1962).
248. J. K. Baker, Mach. Design, **33**, No. 9, 102 (1961).
249. H. Hayashi, Eng. Mater., **8**, No. 12, 110 (1960).
250. L. E. Amborsky and C. J. Mighton, US P. 3 107 198 (1963); Chem. Abs., **60**, 737 (1964).
251. Dutch P. 6 506 632 (1965); Chem. Abs., **64**, 17 869 (1966).

252. Dutch P. 6 407 314 (1964); Chem.Abs., 63, 799 (1965).
253. A. Kudo, Eng. Mater., 10, No. 1, 44 (1962).
254. French P. 1 449 393 (1966); Chem. Abs., 66, 86 746 (1967).
255. R. W. Miller and T. Podnar, Package Eng., 12, 94 (1967).
256. R. D. Blue and M. P. Naipert, US P. 2 944 956 (1960); Chem. Abs., 54, 19 234 (1960).
257. T. Satogawa, Chem. Ind. (Japan), 11, 1073 (1960).
258. H. W. Coover and J. B. Dickey, US P. 2 592 248 (1952); Chem. Abs., 47, 4362 (1953).
259. D. W. Woodward, US P. 2 579 061 (1951); Chem. Abs., 46, 3327 (1952).
260. B. W. Howk and L. Plambeck, US P. 2 499 097 (1950); Chem. Abs., 44, 4723 (1950).
261. B. P. 593 605 (1947); Chem. Abs., 42, 2139 (1948).
262. M. J. Roedel, US P. 2 497 323 (1950); Chem. Abs., 44, 4722 (1950).
263. R. M. Jouce and J. C. Sauer, US P. 2 479 367 (1949); Chem. Abs., 44, 1754 (1950).
264. B. P. 608 807 (1948); Chem. Abs., 44, 1753 (1950).
265. T. A. Ford, US P. 2 468 054 (1949); Chem. Abs., 43, 5638 (1949).
266. W. E. Hanford and J. R. Roland, US P. 2 468 664 (1949); Chem. Abs., 43, 5410 (1949).
267. J. B. Dickey, US P. 2 466 395 (1949); Chem. Abs., 43, 4897 (1949).
268. D. D. Coffman and T. A. Ford, US P. 2 456 255 (1948); Chem. Abs., 43, 1608 (1949).
269. C. A. Thomas, US P. 2 406 717 (1946); Chem. Abs., 40, 7702 (1946).
270. B. P. 592 113 (1947); Chem. Abs., 42, 794 (1948).
271. A. C. Hetherington, US P. 2 866 721 (1958); Chem. Abs., 53, 6650 (1959).
272. P. L. Sbrolli and L. Lucchetti, Materie Plast., 27, 801 (1961).
273. J. B. Dickey, US P. 2 472 811 (1949); Chem. Abs., 43, 6465 (1949).
274. Belg. P. 611 530 (1961); Chem. Abs., 57, 6125 (1962).
275. C. A. Thomas, US P. 2 362 960 (1944); Chem. Abs., 39, 3179 (1945).
276. K. Okamura, T. Satogawa, and M. Joneya, Japanese P. 3390 (1961); Chem. Abs., 55, 21 675 (1961).
277. R. D. Burkhart and N. L. Zutty, J. Polymer Sci., A1, 1137 (1963).
278. Belg. P. 562 701 (1958); Chem.Abs., 53, 10 845 (1959).
279. B. P. 583 482 (1946); Chem. Abs., 41, 2939 (1947).
280. Hideo Tanaka, Kazuo Okamura, Takaomi Satokawa, and Minoru Yoneya, Japanese P. 3395 (1961); Ref. Zhur. Khim., 14P452 (1962).
281. L. Weintraub, J. Hoffman, and J. A. Manson, Chem. Ind., 1963 (1965).
282. Kimziro Sakai, Japanese P. 8581 (1956); Chem. Abs., 52, 9642 (1958).
283. W. J. Smythe and E. Müller, US P. 2 917 473 (1959).
284. E. W. Gluesenkamp and J. D. Calfee, US P. 2 847 401 (1958); Chem. Abs., 52, 21 251 (1958).
285. BRD P. 1 114 279 (1960); Chem. Abs., 56, 4980 (1962).
286. E. S. Lo and G. H. Grawford, US P. 2 992 211 (1961).
287. E. S. Lo, US P. 2 986 556 (1961).
288. J. J. Drysdale, US P. 2 956 988 (1960); Chem. Abs., 55, 6936 (1961).
289. B.P. 946 050 (1964); Chem. Abs., 60, 12 132 (1961).
290. B.P. 949 752 (1964); Chem. Abs., 60, 15 524 (1964).
291. R. N. Haszeldine, R. E. Banks, and H. Sutcliffe, B.P. 979 428 (1965); Chem. Abs., 62, 11 934 (1965).
292. E. L. Martin, US P. 2 396 713 (1946); Chem. Abs., 40, 3936 (1946).
293. E. L. Martin, US P. 2 409 948 (1946); Chem. Abs., 41, 4005 (1947).
294. V. L. Folt, US P. 2 460 573 (1949); Chem. Abs., 43, 2818 (1949).
295. Kh. U. Usmanov, A. A. Yul'chibaev, and M. K. Asamov, Uzbek. Khim. Zhur., 12, No. 4, 56 (1968).
296. Kh. U. Usmanov, A. A. Yul'chibaev, and Kh. Yuldasheva, Uzbek. Khim. Zhur., 11, No. 2, 27 (1967).
297. R. O. Osborn, BRD P. 1 238 204 (1957); Chem. Abs., 67, 65 153 (1967).
298. J. R. Semancik and W. A. Gallup, US P. 3 325 344 (1967); Chem. Abs., 67, 65 029 (1967).
299. D. Sianesi and G. Caporiccio, French P. 1 478 785 (1967); Chem. Abs., 67, 109 161 (1967).