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Vinyl Fluoride Polymers

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Results obtained on the polymerisation, copolymerisation, and graft copolymerisation of vinyl fluoride, various properties of the polymers thus produced, and also possible fields of application are discussed on the basis of 435 references published up to the beginning of 1976

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I. INTRODUCTION

The polymerisation and copolymerisation of vinyl fluoride, as well as various properties of the resulting polymers, have been very intensively studied during recent years. Poly(vinyl fluoride) possesses good heat resistance, thermal stability, and chemical inertness, while being readily processed. Films of this polymer are distinguished by high mechanical strength, durability, flexibility, transparency, and enhanced resistance to the atmosphere and to light. Several copolymers and graft copolymers possess similar qualities. In virtue of these valuable properties polymers based on vinyl fluoride are currently among the principal types of fluorinated polymers widely employed in various branches of modern technology, building construction, agriculture, and everyday life.

A few review papers have been published on vinyl fluoride and its polymers [1-3], a subject that has been partly covered also in several books [4-6]. However, attention is paid in these publications mainly to the preparation and properties of vinyl fluoride itself, with little space devoted to the synthesis of its polymers and their properties. Moreover, they contain no results published during the past 4–5 years.

II. POLYMERISATION OF VINYL FLUORIDE

Vinyl fluoride was prepared as early as 1901 by Swarts [7], but its polymerisation was accomplished only in 1934. [8] Quite detailed information both on the kinetics of the polymerisation of vinyl fluoride and on the properties of the polymer was published in 1946 by Newkirk [9].

Vinyl fluoride is more difficult to polymerise [8,10] than are e.g. vinyl chloride, vinylidene chloride, and vinylidene fluoride, owing to the appreciable inertness of the double bond and the great activity of vinyl fluoride radicals. The process is therefore very sensitive to the presence of impurities that may inhibit polymerisation [8,11-14]. The failures and difficulties met by the early investigators in their attempts to polymerise vinyl fluoride were due mainly to inadequate purity of the monomer, although the low reactivity of the double bond in vinyl fluoride was also quite important. The diminished activity of the double bond was due to a mesomeric effect weakening the inductive effect of the fluorine atom [15-18].

The successful development during recent years of methods for obtaining vinyl fluoride in a high state of purity has enabled its free-radical polymerisation to be achieved both by chemical initiation and under the influence of radiation.

1. Chemically Initiated Polymerisation of Vinyl Fluoride

Various organic peroxides have been most widely used to initiate the polymerisation of vinyl fluoride. Newkirk [9] obtained poly(vinyl fluoride) of density 1.39 g cm^{-3}, soluble in hot dimethylformamide, in dioxan, chlorobenzene, and several other solvents, by employing benzoyl peroxide as initiator. This polymerisation initiator was used also by other workers [12,19-23]. Other peroxides that have been widely used to polymerise vinyl fluoride are acetyl, diethyl, di-t-butyl [12], isobutyl [25], lauroyl [24,26], and polyperfluoropropylene, as well as t-butyl hydroperoxide [27].

The polymerisation of vinyl fluoride in the presence of peroxide initiators is strongly inhibited by oxygen [12]. Acetylene has a similar effect: the yield of poly(vinyl fluoride) in the presence of 2% of acetylene does not exceed 3%. [10,22] Polymerisation in the presence of 2.5% of 1,1-difluoroethane, initiated by benzoyl peroxide, gave a normal yield [12]. Traces of propene help to control the molecular mass, and the resulting polymer has a constant melt flow index [28].

The influence of benzene, methanol, propan-2-ol, and 1,3-dioxolan on the polymerisation of vinyl fluoride was studied [12]. All the organic solvents examined interacted with the monomer, and thus caused a sharp decrease in the molecular mass of the resulting polymer. This is shown especially clearly in the polymerisation of vinyl fluoride in tetrachloromethane in the presence of a peroxide [29]. The telomerisation of vinyl fluoride by chloroformates [30], iodotrifluoromethane [18], perfluorochloroalkenes [31], and perhalogenoethanes [32] has been studied in the presence of peroxides. The telomers obtained are used as plasticisers for poly(vinyl fluoride); they do not bleed and do not cause opacity in the polymer when bent [18].

Polymers of higher molecular mass are formed in the presence of water than in the presence of acetone [33,34].

Initiation of polymerisation by benzoyl or lauroyl peroxide in a fluorinated solvent—1,1,2-trichlorofluoroethane or iodotrifluoromethane—gave poly(vinyl fluoride) soluble in hot dimethylformamide[18]. A polymer of high molecular weight is formed also when the peroxide of a fluorinated acid[35] or trifluoromethyl peroxide[36] is used as initiator.

Two-stage polymerisation in aqueous suspension in the presence of benzoyl peroxide was suggested[37] for the preparation of light-resistant poly(vinyl fluoride). Processes were also developed for the continuous polymerisation of vinyl fluoride in aqueous suspension[38,39] and methods for separating the resulting polymer from water, which was subsequently recycled[28,37,39]. The polymerisation of vinyl fluoride was studied in the presence of various surface-active agents and stabilisers of suspensions—methylcellulose[40-42], glucose ethers and esters, water-soluble copolymers of ethylene, 2-ethylhexyl acrylate, and 2-ethylhexyl methacrylate[43], and also copolymers of vinyl acetate and allyl alcohol with maleic acid or anhydride[44].

Emulsion polymerisation had been most widely used for the preparation of poly(vinyl fluoride) used especially in coatings. Water alone or mixed with organic solvents was the dispersion medium[21,26,45-47]. The emulsifiers were magnesium dodecanesulphonate[40], sodium ditridecyl sulphosuccinate[27], sorbitol ethers or esters, or C_{12-18} aliphatic acids[48].

As the polymerisation of vinyl fluoride in the presence of the usual peroxide initiators requires temperatures above 50°C and hence high pressures, the possibility of polymerisation at relatively low temperatures and pressures has been intensively examined during recent years. Use of various alkyl peroxodicarbonates as initiators has proved especially fruitful for this purpose. A most detailed study has been made of the polymerisation of vinyl fluoride in the presence of the di-isopropyl ester[21,49-53]. As the ester content increases from 0.28 to 0.98 wt.% on the weight of the monomer the rate of polymerisation in heptane solution increases in conformity with the equation $v = kc^{0.58}$, where k is the overall polymerisation rate constant and c the initiator concentration; the corresponding equation when the concentration of vinyl fluoride in heptane solution increases from 3.07 M to 9.20 M is $v = kc^{0.60}m^{1.10}$, in which m is the monomer concentration.

The activation energy of polymerisation is ~17 kcal mole^{-1}. Methylcellulose[54], poly(vinyl alcohol)[55], and mixtures of water-soluble cellulose ethers and partly hydrolysed poly(vinyl acetate)[48] have been suggested as peptising agents for the suspension polymerisation of vinyl fluoride in the presence of di-isopropyl peroxodicarbonate. In order to improve the compatibility of poly(vinyl fluoride) with plasticisers the suspension polymerisation of vinyl fluoride is conducted in the presence of 0.05–2% (on the weight of the monomer) of carboxymethyl-, hydroxypropyl-, or hydroxyethyl-cellulose[56,57].

The emulsifiers used in the emulsion polymerisation of vinyl fluoride are dodecyl benzenesulphonate[54] and such non-ionogenic surface-active agents as alkyl or alkylphenyl ethers or esters of polyoxyethylene and polyoxypropylene[58], sorbitol and its ethers, and also esters of C_{12-18} aliphatic acids[48]. Not only di-isopropyl peroxodicarbonate but also the dipropyl ester[59] and didecanoyl peroxide[26] have been used for the emulsion polymerisation of vinyl fluoride. An 85% yield of poly(vinyl fluoride) is obtained when polymerisation is initiated by 0.05–1.0 mole % of bis-2-t-butylcyclohexyl peroxodicarbonate[60].

The polymerisation of vinyl fluoride at ordinary temperatures and pressures can also be initiated by various redox systems, among which the most efficient are organoelementary compounds in the presence of oxygen, e.g. alkylboranes at 25–40°C.[23,26,61] The activation energy of polymerisation depends on the nature of the group in the alkyl borane: it is 6 and 15 kcal mole^{-1} for triethylborane and tri-isobutylborane respectively. With increase in the ratio of molecular oxygen to the trialkylborane the rate of polymerisation passes through a maximum. Rise in temperature increases the probability of the formation of groups such as $CH_2.CHF.CHF.CH_2$.[18]

A kinetic study of the polymerisation of vinyl fluoride has been made in the presence of tri-n-butylborane[53,62]. The reaction velocities are given by the equations $v = kc^{0.61}$ and $v = kc^{0.65}m^{1.24}$ in the mass and in ethyl-acetate solution respectively. The activation energy of polymerisation is 10 kcal mole^{-1}. Polymer samples of crystallinity <30% are obtained by using as initiators organoboron compounds of the type BR_3 (where R represents a C_{1-12} group) or RR'BX (where X = OR) with oxygen[63-66], and their coordination compounds with ammonia, hydrazine, hydroxylamine, and amines[67-71]. Trialkylboranes with hydrogen peroxide in the molar proportions 0.05–0.6 are also effective initiators[72,73].

Vinyl fluoride can be polymerised at ordinary temperatures by the use not only of alkylboranes but also of triethylaluminium, di-isopropylcadmium, diethylcadmium, di-isopropylzinc, diethylzinc, ethylzinc isobutoxide, or butylethylzinc in the presence of oxygen or a peroxide, e.g. benzoyl peroxide, 1-hydroxycyclohexyl peroxide, or cyclohexyl hydroperoxide[19,74]. The binary systems formed by diethylaluminium bromide or triethylaluminium with titanium tetrachloride[75,76] and by tri-isopropylaluminium with tetraisopropoxytitanium[77] have been tested. In the presence of tetraethyl-lead with sodium persulphate vinyl fluoride underwent polymerisation only at high temperatures and pressures (40–100°C above 150 atm)[78].

Heterogeneous catalysts comprising aluminium alkyls and titanium or vanadium halides proved ineffective for the polymerisation of vinyl fluoride[79,80]. However, soluble halogen compounds of vanadium combined with aluminium mono- or di-alkyls in the presence of polar solvents, e.g. vanadium acetylacetonate and an alkylalkoxyaluminium chloride in dimethylformamide, initiate the polymerisation of vinyl fluoride very vigorously at 20–50°C.[81] The activation energy of polymerisation fluctuates from 11 to 16 kcal mole^{-1} depending on the nature of the radical R attached to the aluminium atom. Manganic acid and various of its salts are effective initiators of the polymerisation in aqueous suspension[82].

The systems formed by potassium peroxodisulphate with sodium sulphite and with sodium hydrogen sulphite have also proved effective[83]. In their presence vinyl fluoride undergoes emulsion polymerisation at relatively low temperatures (50–60°C), the resulting polymer does not settle on the walls, and it is readily removed from the reaction vessel.

With azo-compounds as initiators the polymerisation of vinyl fluoride is usually conducted at temperatures of 50–100°C and pressures exceeding 30 atm.[84] Thus in the presence of α-azoisobutyramidine[85,86] polymerisation takes place in aqueous medium at 70–90°C and 30 atm. A continuous process has been developed for polymerisation in aqueous suspension initiated by α-azoisobutyramidine hydrochloride[12,29,38,87-89]. 2,2'-Diguanyl-2,2'-azopropane dihydrochloride[28,37,39,90,91], 2,2'-diguanyl-2,2'-azobutane dihydrochloride, and azo-α-cyclopropylpropionamide hydrochloride[92] have also been used for this purpose. Polymerisation of vinyl fluoride has been initiated also by

$\alpha\gamma\gamma'$-trimethyl- and $\alpha\gamma$-dimethyl-α-azovaleronitrile[93], 1-azocyclohexanecarbonitrile, γ-ethyl-γ'-hydroxyethyl-azobutyronitrile, and azo-disulphonates of alkali and alkaline-earth metals[45]. The most commonly used initiator for the polymerisation of vinyl fluoride has been azoisobutyronitrile[12,53,64,93,94], when the order of reaction with respect to the initiator is 0.55 in the mass.

2. Polymerisation of Vinyl Fluoride by Irradiation

When exposed to ultraviolet radiation in the absence of a sensitiser, vinyl fluoride does not polymerise but decomposes into acetylene and hydrogen fluoride[95], which is eliminated by a molecular mechanism. In the early work[9] polymerisation was effected by ultraviolet exposure in the presence of benzoyl, lauroyl, or acetyl peroxide in a quartz capillary. Several other publications appeared later[33,34,96]. Thus exposure of vinyl fluoride in acetone solution to ultraviolet radiation of wavelength 2537 Å at 27°C for 8 h gave 36% of the polymer[33,34].

The polymerisation of vinyl fluoride under the influence of cobalt-60 γ-rays has been studied in the greatest detail[97-109]. The first reports of the possibility of the radiation polymerisation of this monomer appeared as early as 1962–1963.[99-102] The laws governing such polymerisation in the mass, in the gas phase, and in the presence of various solvents have now been investigated in detail.

The polymerisation of vinyl fluoride in the mass has been conducted at dosage rates of 13–100 rad s^{-1}.[103] At and above 70 rad s^{-1} the rate curves have a well developed sigmoid form, which is attributed to heterophase occurrence of the process. The rate of polymerisation passes through a maximum at a polymer yield of 45–65%. In the mass at 38°C the rate of polymerisation is proportional to the dosage rate to the power 0.42. The radiation-chemical yield lies in the range 8000–30 000 mol./100 eV, as a consequence of the chain character of the process.

Under the influence of γ-rays vinyl fluoride polymerises at less than half the rate for vinylidene fluoride and trifluoroethylene, but more rapidly than chloro-trifluoroethylene, hexafluoropropene, and perfluoroisobutene[110]. As with chemical initiation, the radiation polymerisation of vinyl fluoride is strongly inhibited by oxygen and by acetylene[99,111]; increasing the acetylene content of the monomer from 0.5% to 1% diminishes the rate of polymerisation almost to one-third.

In the first study of the gas-phase polymerisation of vinyl fluoride[112,113] irradiation with cobalt-60 γ-rays was employed at dosage rates of 10, 20, 70, and 100 rad s^{-1}. The increase from 10 to 100 rad s^{-1} increases the rate of polymerisation from 1.29 to 22–23 g $litre^{-1}$ h^{-1}. Such a sharp increase is attributed to generation by the radiation of active centres in the product, polymerisation at which results in branched polymers. The radiation-chemical yield lies between 1670 and 15 670 mol./100 eV.

Detailed studies have been made also of the radiation polymerisation of vinyl fluoride dissolved in tetrachloromethane, benzene, dimethylformamide, dichloroethane[114,115], and a series of fluorinated hydrocarbons[116-118]. In the presence of tetrachloromethane the rate of polymerisation passes through a maximum at a monomer concentration of 0.80 M, exceeding by 50% the rate in the mass. With an initial monomer concentration of 0.26–0.35 M a colourless, viscous, oily product of molecular weight 320–540 is formed. Mole fractions of vinyl fluoride of 0.77 and above yield a solid polymer. The constant of chain transfer to tetrachloromethane is 0.0196. The infrared spectra[119] exhibit maxima in the regions of 790 and 712 cm^{-1}, indicating partial incorporation of the trichloromethyl group into the poly(vinyl fluoride) macromolecules.

The relative rate of polymerisation of vinyl fluoride is strongly dependent on the nature of the solvent[115]. Thus in benzene the rate drops sharply, and in dimethylformamide it is almost a linear function of the monomer concentration, but in dichloroethane the rate is higher than in the mass. Such variation in the rate of polymerisation of vinyl fluoride is due both to differences in the radiation-chemical yields of radicals from these solvents and to a redistribution between monomer and solvent of the energy absorbed from the radiation.

The dependence of the rate of the radiation polymerisation of vinyl fluoride on the dosage rate I and the monomer concentration is described by different equations: in benzene $v = kI^{0.73}m^{2.7}$; in dimethylformamide $v = kI^{0.76}m^{2.2}$; in dichloroethane $v = kI^{0.86}m^{1.2}$; and in tetrachloromethane $v = kI^{0.80}m^{1.2}$. The activation energies of radiation polymerisation in the mass, in dimethylformamide, in dichloroethane, and in tetrachloromethane are respectively 5.7, 4.8–5.3, 5.5–6.1, and 5.0–5.5 kcal $mole^{-1}$ depending on the solute concentration. These values are 10–11 kcal $mole^{-1}$ smaller than the activation energy in the presence of material initiators, which is one of the advantages of radiation polymerisation.

Vinyl fluoride has been polymerised also in a plasma[120].

III. STRUCTURE AND PROPERTIES OF POLY(VINYL FLUORIDE)

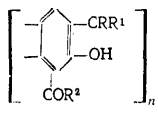
Poly(vinyl fluoride) gives relatively sharp X-ray diffraction patterns[121-124]. The crystallinity of specimens lies in the range 35–47% depending on the conditions of preparation. The unit cell possesses hexagonal symmetry. The macromolecules, like those of polyethylene or polyvinyl alcohol, have a planar zigzag conformation[65]. The interplanar spacing is 4.95 Å, and the repeat distance along the chain is 2.53 Å.[125,126].

One of the main factors determining many properties of poly(vinyl fluoride) is the sequence in which one unit is added to another in the macromolecule. "Head to tail" addition of monomer units was noted at an early stage by Newkirk[9]. Groupings of the CHF.CHF type, resulting from "tail to tail" addition, have been identified[127] in the nuclear magnetic resonance spectra. Bovey et al.[128] established by high-resolution n.m.r. spectroscopy the presence of a resonance line having a chemical shift of 8.33 ppm (on the τ scale), which may be due to "head to head" structures. The possibility of the presence of such units in the polymer chain is admitted by other workers who have studied the infrared and n.m.r. spectra of this polymer[129-135].

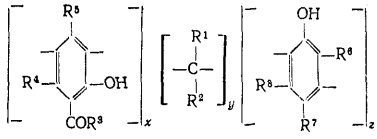
A distinguishing feature of poly(vinyl fluoride) is its great photostability[136], which is due to the complete transparency of its films in the ultraviolet and visible regions of the spectrum. Thus transparent films remained colourless and retained 50% of their original tensile strength after exposure to sunlight for 10 years[122]. Films 0.13 mm thick transmit >90% of radiation in the wavelength range 2350–1950 Å.[137]

Because of this great transparency, however, articles coated with such films are not always effectively protected from the action of ultraviolet radiation. Ultraviolet-absorbers must be introduced into the film, widely used

examples being triazoles [138,139], polymers of acrylic derivatives of acetophenones or benzophenone [140,141], polymers of general formula [142]



($R = R^1 = H$, $R^2 = C_6H_5$, and $n = 2$ or 3), and linear polymers having the structure [143]



(R^1 and R^2 = H, C_{1-6}-Alk, chloroalkyl, furyl, vinyl, propenyl, or phenyl; $R^3 = C_{1-6}$-Alk or Ar; and R^4, R^5 = H, OH, Hal, Ar, aryloxyalkyl, or cyclohexyl). The same purpose can be achieved also by copolymerising [144] vinyl fluoride with a small quantity of the acrylic-acid derivative $CH_2:CR.COO.C_6H_4.CO.CH_2.CO.R'$ (R = H or C_{1-3}-Alk and $R' = C_{1-18}$-Alk or substituted phenyl). Other proposed ultraviolet-absorbers are benzophenone [146] †, various hydroxy-derivatives thereof [147-150], and the polyester obtained from adipoyl dichloride and 2,4,4'-trihydroxybenzophenone [151,152].

Poly(vinyl fluoride) films possess extremely good mechanical properties. Great strength is combined with elasticity and resistance to multiple bending even at low temperatures [122]. These properties are only slightly impaired by the prolonged action of water vapour [153]: thus at 99°C no appreciable deterioration in the elongation of films and their stability on multiple bending had occurred after 100 h. The films are characterised also by enhanced abrasion resistance [154-158], in which they are inferior only to polytetrafluoroethylene [159]. This property is fully consistent with the swellability, wettability, and surface free energy of poly(vinyl fluoride) [160].

Poly(vinyl fluoride) possesses great chemical resistance. The stability of the physical structure of films and their characteristic resistance to oxidation and hydrolysis were studied from the variation in properties on ageing in moist and dry atmospheres at high temperatures [122]. During ageing the tensile strength of a highly oriented film approaches that of films having less orientation of the molecules [161]. The polymer is stable towards caustic soda, hydrochloric and sulphuric acids, and primary and secondary amines [161,162]. It far surpasses in chemical stability poly(ethylene terephthalate), and is not inferior to a polyamide film. Treatment with nitrogen trifluoride or monofluoride at 80–100°C leads to the formation of cross-links in poly(vinyl fluoride) and improves the mechanical properties of the film [163,164]. The polymer can be chlorinated [165] and fluorinated [166] by the action of the gaseous halogens.

The product of the chemically initiated polymerisation of vinyl fluoride at temperatures above 100–110°C dissolves in such strongly polar solvents as *N*-substituted amides, dinitriles, thiolan dioxide, tetramethylurea, *N*-methylpyrrolidone, and γ-butyrolactone [12], the polymer separating out when the solution is cooled below 100°C. At room temperature poly(vinyl fluoride) dissolves well in hexamethylphosphoramide [167-169], perfluoropropane-2,2-diol, and 1,3-dichloro-1,1,3,3-tetrafluoropropane-2,2-diol [170]. The product of radiation polymerisation is considerably less soluble [171]. The conditions of preparation—dosage rate and radiation dose, temperature, presence of impurities and additives, and state of aggregation of the monomer during polymerisation—than have a marked effect on the solubility of the polymer. The solubility in boiling solvents of polymer samples obtained in the mass is respectively 30–35%, 22–27%, 10–15%, and 1–5% in dimethylformamide, hexamethylphosphoramide, cyclohexanone, and dioxan respectively [97]. Gas-phase polymerisation yields a product of enhanced solubility [113], and a polymer obtained in tetrachloromethane dissolves still better [172].

Because of the poor solubility of poly(vinyl fluoride) simple and reliable methods for determining its molecular mass were lacking until recently, so that only estimates were available [9,12,22]. In the first detailed study of the properties of solutions in dimethylformamide quantitative relations were deduced for determining the molecular mass and other characteristics of the polymer. The specimens used had been obtained in the presence of 0.003–0.2% of azoisobutyramidine at 67–97°C. The weight-average molecular mass of 9 samples studied varied from 143 000 to 654 000, and the number-average value from 76 400 to 218 000. The relation between the intrinsic viscosity and the molecular mass was given by $[\eta] = 6.42 \times 10^{-5} M_S^{0.80}$. More recently [50] molecular masses have been determined and the molecular-mass distribution has been studied for samples of the polymer obtained in the presence of α-azoisobutyronitrile, di-isopropyl peroxodicarbonate, and tributylboron monoperoxide as initiators, when the resulting polymer solutions had intrinsic viscosities of 1.58, 1.75, and 1.20 dl g^{-1} respectively.

All the solvents for poly(vinyl fluoride) contain both groups that solvate the hydrocarbon portion and groups that interact with the polar part of the monomer units. Since interaction is probably of the nature of hydrogen bonding, the possibility of the latter must be taken into account in studying the interaction of various solvents with the polymer. It was established [174], for example, that replacing a hydrogen atom in polyethylene by a fluorine atom enhances its wettability by polar liquids capable of forming hydrogen bonds, whereas its wettability by non-polar liquids diminishes. A film of poly(vinyl fluoride) possesses relatively slight permeability to gases [175-177]. Its permeability to the vapours of organic solvents is also insignificant, except in the case of ketones, which probably cause the polymer to swell [178].

Sivadjian and his coworkers found [179] that at 25°C the water permeability of poly(vinyl fluoride) films is fourfold that of polyethylene, and sevenfold that of a Kel-F film. The probable reason is the possibility of free rotation of monomer units and larger segments in the crystal lattice of poly(vinyl fluoride) [137,162].

In its adhesive properties poly(vinyl fluoride) surpasses polytetrafluoroethylene by a factor of 4 and approaches polyvinyl alcohol [180]. Because of the vigorous growth in its application as a coating on various articles, however, various methods for improving its adhesive properties have recently been widely studied. In particular, this has been achieved by impregnating the surface

† Reference 145 appears to be missing and out of context: it is concerned with the heat-treatment of polymer films (Ed. of Translation).

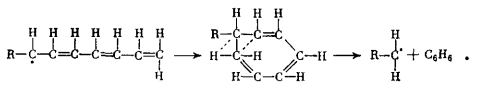
of a film of the polymer with a thermosetting resin[93] or by activating it by means of an electric discharge in the presence of such electrophilic substances as boron trifluoride, aluminium trichloride, chlorine, fluorine, etc.[168,181] The adhesion of a film of the polymer was improved also on bombardment with helium or hydrogen atoms[182]. The adhesion of a film was increased by factors > 100 when the surface was treated with substances capable of abstracting hydrogen and fluorine atoms, such as boron trifluoride, its hydrates, or etherates in the gas or liquid phase in the presence of oxygen at normal or elevated temperatures[161,162,183-185]. The adhesive properties of a poly(vinyl fluoride) film can be improved by treating its surface with a flame[186], nitrogen, an activated plasma[187], a diazo-compound[71,188-190], concentrated sulphuric acid, or hot alkali[191]. Polyurethanes[192] and polyamides[193] have been deposited on the film surface for the same purpose. In several cases adhesion is improved by modifying not the film itself but the metal surface to which the film adheres[186,194]. Thus treating an aluminium surface with a solution of trishydroxyethylamine increases the adhesion of a film of the polymer from zero to 1.1 kg.

Poly(vinyl fluoride) belongs to a class of polymers characterised by high melting points (197°C)[12,22] with relatively low heats of fusion, as follows from its thermodynamic parameters[93]—ΔH_M = 1800 cal mole^{-1} and ΔS_M = 3.87 cal mole^{-1} deg^{-1}.

This polymer is characterised also by great thermal stability, a consequence of the strength of the carbon–fluorine bond, the regularity of structure of the main chain, and the high energy of interchain interaction. The thermal stability depends on the method and conditions of preparation of the polymer. The product of free-radical initiation in the mass begins to decompose in a vacuum at 300°C, and in air at 170°C,[195] with respective activation energies of 44.0 and 21.0 kcal mole^{-1}. Thermal breakdown of the product of emulsion polymerisation begins in a vacuum at 290°C, with an activation energy of 51.0 kcal mole^{-1}.

The thermal stability of poly(vinyl fluoride) prepared by the radiation method has been studied in the greatest detail[195-198]. The polymer obtained in the mass begins to decompose in a vacuum above 300°C, and in air at 175°C, the activation energy being respectively 61.1 and 24.0 kcal mole^{-1}.[197] The product of gas-phase polymerisation begins to decompose at 300°C,[196] like that obtained in the mass. With further rise in temperature, however, the former polymer undergoes more intense breakdown than does the latter. The activation energy of degradation is also lower in the first case: 36.0 and 20.0 kcal mole^{-1} in a vacuum and in air respectively. The enhanced thermal stability of the polymer obtained in the mass by the radiation method is explained both by its great purity and by the partial formation of three-dimensional structures during polymerisation.

The main product of the decomposition of poly(vinyl fluoride at 310–325°C is hydrogen fluoride[199-203]. Further rise in temperature changes the composition of the degradation products: at 332°C they comprise 10 components, and at 350°C about 13 components[198]. The infrared spectra of the polymeric residues show[198] that they consist of macromolecules cross-linked one to another and containing conjugated and isolated double bonds together with fused aromatic structures. It has been suggested that the elimination of hydrogen fluoride in the thermal degradation of poly(vinyl fluoride) takes place by a molecular mechanism. The presence of considerable quantities of benzene among the decomposition products is explained[198] as a result of secondary decomposition, probably following the formation and isomerisation of polyene radicals:



Toluene and xylene are formed similarly.

In spite of the enhanced stability of poly(vinyl fluoride) its successful processing and use of the resulting articles under various conditions require at present that it should be stabilised by means of various compounds[200]. These agents should meet various requirements[199]: (i) they should be good acceptors of hydrogen fluoride; (ii) they should be dienophilic, i.e. capable of Diels–Alder reactions; and (iii) they should possess antioxidant properties. Amines and amides containing mobile hydrogen atoms[203], glycerol monolaurate[204], and salicylate salts containing one or two substituents in the benzene ring[205] have been proposed as stabilisers for poly(vinyl fluoride). Substituted 1–8-octahydro-6-methylenenaphthalenes proved to be highly effective stabilisers[206]; they also lower the viscosity of the polymer melt, are fully compatible with it, and are insoluble in water. Terpenes, thiols, and disulphides are used as stabilisers when a film of the polymer is formed by extrusion[207]. Alkyl(C_{2-6}) hydrogen fumarates and maleates raise to 250°C the temperature at which poly(vinyl fluoride) begins to decompose in air[208].

Other compounds that can be used as thermal stabilisers are urea and its derivatives[209], 1,1-diphenylcyclohexane-*pp'*-diol[210,211], thiobismethyl-t-butylphenol[212], terpenes and certain alkenoylamides and alkenoyloxyphenylbenzotriazole-containing polymers[207], polyvinylpyridine[213], polymers of *ortho*-hydroxylated and *para*-substituted phenol[214], 2,2'-thiobisalkylphenols, phenoxides, or salts of a carboxylic acid of a bivalent organometallic phosphite and tin 2-ethylhexanoate, dialkyl pentaerythritol phosphites or their mixtures, polyhydroxylated compounds either pure or combined with sulphur- or phosphorus-containing compounds[215], and compounds of type Zn(S.$PSR_2)_2$, where R is an aliphatic (normal or branched), cyclic, or aromatic radical containing 2–18 carbon atoms[216].

Copolymerisation of vinyl fluoride with bicyclo[2,2,1]-heptadiene[214] will raise by 20 deg the temperature at which poly(vinyl fluoride) begins to decompose. Alkali-metal formates are effective thermal stabilisers for the polymer. The potassium and sodium salts have proved the best[198]: addition of 0.5% of potassium formate raises to 270°C the start of decomposition; similar results are obtained with sodium formate. Certain cross-linking agents, such as amines, ammonia[217], and *cis*-dinitrogen difluoride, are suitable for improving the thermal stability of the polymer[164].

Poly(vinyl fluoride) differs from polytetrafluoroethylene and polychlorotrifluoroethylene in possessing high radiation resistance[218,219]. Whereas ionising radiation depolymerises the second polymer with cleavage of carbon–carbon bonds in the chain, poly(vinyl fluoride), as a polymer containing hydrogen, is cross-linked. Films of the latter remain unchanged at radiation doses up to 32 Mrad, whereas a polytetrafluoroethylene film becomes appreciably shorter even with a dose of 8 Mrad.[26] Irradiation with cobalt-60 γ-rays liberates various gaseous products, mainly hydrogen fluoride[220], the rate of evolution of which depends on the dosage rate in conformity with the equation $v = kI^{0.55}$. Exposure lowers the flow point of the polymer considerably[221], which is attributed to partial degradation

of chains, amorphisation of the polymer, the plasticising effect of simple substances formed by radiolysis, and the decrease in the energy of intermolecular interaction due to the decrease in polar groups.

Study of the relaxation properties of the polymer has begun only recently. Specimens obtained in different ways exhibit structural transition temperatures of −70.43 [−70 to −43 (?) (Ed.of Translation)], 125−150, and 195−235 °C.[49, 221] In order to interpret the mechanism of these transitions, a method of forced resonance vibrations was used to examine the dynamic mechanical properties of the polymer[221]. The temperature dependence of the dynamic Young's modulus E and the mechanical loss factor $\tan\delta$ correlate well with the above values. The stress−strain curves are peculiar in character[49]: the polymer breaks without necking even at temperatures up to 80 °C. The curves do not exhibit a region of rubberlike elasticity.

Pure poly(vinylfluoride) melts in air with partial decomposition. The introduction of various plasticisers to lower the melting point is therefore of direct practical interest for its processing into films, sheets, and fibres. An investigation[222] of plasticisation within and between blocks used as plasticisers dimethyl, diethyl, dibutyl, and dioctyl phthalates, tritolyl phosphate, butyl stearate, castor oil, and fluorinated hydrocarbon oils. A specimen of the polymer containing 25−30% of dibutyl phthalate does not undergo degradation cross-linking and flows irreversibly at 165 °C. Similar results have been obtained for other plasticisers. Different methods of polymerisation result in different effects of plasticisation, which is more efficient for specimens obtained by the suspension method than by other processes. The tensile strength of the plasticised polymers[223] passes through a maximum when containing 5−6% of dioctyl phthalate, 2% of castor oil, or 1% of butyl stearate. In contrast, the elongation of the specimens at break passes through a minimum. X-Ray diffraction shows[223] that the crystallinity increases on the introduction of up to 2% of a plasticiser, owing to increased mobility of the chains, but begins to diminish with further increase in the plasticiser content.

The combination of good electrical properties with enhanced thermal stability, chemical inertness, photostability, and adhesive properties makes poly(vinyl fluoride) one of the first choices for use in electrical insulation[224]. In contrast to many polymers, the rate of charge accumulation is independent of the applied voltage and the ambient humidity[225], because of the low hygroscopicity of the polymer. Surface films are coated with bishydroxyalkylamides to prevent the accumulation of static charge[226,227]. The dielectric constant and the dielectric losses are tenfold those for the corresponding polymeric chloride and bromide[228-230]. The dielectric constant usually increases with rise in temperature, but diminishes with increase in frequency[231]. The reason is that, because of the comparatively small radius of the fluorine atom, the polymer chains, are able to perform rotational movements (of small amplitude) in which the monomer units rotate, which can be regarded as segmental motion[232-234].

IV. COPOLYMERISATION OF VINYL FLUORIDE

Methods of preparation analogous to those used for poly(vinyl fluoride) have produced many diverse copolymers with novel properties of practical value.

The copolymerisation of vinyl fluoride with ethylene was first studied by Coffman[235,236], and later by Roedel[237], in the presence of carboxylated initiators over the range 50−150 °C. A more detailed investigation was made by Burkhart et al.[27,238] in the presence of various peroxides and by means of radiation at 160 °C and 100 atm. The copolymers were in all cases enriched with ethylene, independently of the ratio of the monomers in the initial mixture. A copolymer suitable for the production of films and fibres was obtained by conducting the process in solution and in suspension[239,240]. The initiators used were tri-isobutylboron, triethylboron monammine, sodium peroxodisulphate, iron(III) hydrogen sulphate, alkylalkoxyaluminium chlorides, benzoyl peroxide, and di-isopropyl peroxodicarbonate with molecular oxygen. The radiation copolymerisation of vinyl fluoride with ethylene was also studied[241].

Products of diverse properties are obtained by copolymerising vinyl fluoride[242-245] with propene, isobutene, bicycloheptane[246], and styrene[239,247]. A copolymer of vinyl fluoride with vinyl chloride was obtained by Thomas[11] as early as 1944, and was one of the first copolymers of vinyl fluoride. Copolymers with vinyl chloride suitable for the production of films, fibres, and coatings have been prepared by the use of benzoyl peroxide[11], organoboron initiators[247,248], di-isopropyl peroxodicarbonate[249,250], sodium persulphate, iron(II) salts[64,66,247,251-255], and catalysts of Ziegler−Natta type[247].

The radiation copolymerisation of vinyl fluoride with vinyl chloride has been studied in the greatest detail[256-263]. Under otherwise similar conditions the rate of copolymerisation is considerably lower than the rate of separate polymerisation of either component. Copolymers containing up to 50 mole % of vinyl fluoride are completely soluble in dimethylformamide, dioxan, cyclohexanone, 1,1-dichloroethane, and butan-2-one, but those having a higher content of the fluoride are only partly soluble at the boiling points of these solvents. They are transparent to ultraviolet radiation, but absorb strongly in the infrared[257]. The presence of vinyl fluoride units in the copolymers leads to the appearance of infrared absorption bands in the range 1035−1175 cm^{-1}. Ultraviolet exposure results in new infrared bands in the region of 1610, 1700, and 1720 cm^{-1}, which can be assigned to vibrations of the carbonyl group and of isolated and conjugated ethylenic bonds[258]. However, the bands at 690 and 1175 cm^{-1}, due to vibrations of carbon−chlorine and carbon−fluorine bonds respectively, become weaker.

Copolymers of vinyl fluoride and chloride are more wear-resistant than poly(vinyl chloride)[259]. Heat-treatment at 150 and 175 °C causes loss of fluidity owing to cross-linking of the macromolecules. The losses in weight in a vacuum at 200 °C are respectively 36%, 15%, and 9% for poly(vinyl chloride) and copolymers containing 12.1 and 21.6 mole % of vinyl fluoride[261]. The respective activation energies of thermal decomposition are 27.5, 30.2, and 37.5 kcal $mole^{-1}$: i.e. increase in the proportion of vinyl fluoride in the copolymer is accompanied by a parallel improvement of thermal stability. Copolymers obtained by the radiation method were thermally more stable than those resulting from chemical initiation. Thus for a copolymer containing 21.9 mole % of vinyl fluoride the loss in weight in a vacuum at 250 °C for 6 h was 35% and 46% for samples obtained by means of radiation and chemically.

The copolymerisation of vinyl fluoride with vinylidene chloride has been initiated by various peroxides[239,247] and organoboron compounds[239] in solution or in aqueous suspension in the presence of a dispersing agent. Kinetic study of the copolymerisation in the presence of di-iso-

propyl peroxodicarbonate[260] has revealed certain laws: initially the yield of copolymer is a linear function of time, and the rate of copolymerisation is proportional to the initiator concentration to the power 0.53; at high degrees of conversion the rate curves are sigmoid; and the copolymers are enriched with vinylidene chloride whatever the ratio of the monomers in the initial mixture.

The copolymerisation of vinyl fluoride with tetrafluoroethylene can be initiated by peroxides[240,246-266], organoboron catalysts[267], and di-isopropyl peroxodicarbonate dissolved in benzene, chloroform, or dimethylformamide[65]. The copolymer containing 85 mole % of vinyl fluoride has a glass point of 212–213°C; it is soluble in cyclohexanone and dimethylformamide[19].

Copolymerisation of vinyl fluoride with chlorotrifluoroethylene has been accomplished in the mass, in solution, and in suspension in the presence of benzoyl peroxide, di-isopropyl peroxodicarbonate, organoboron compounds, and also sodium persulphate and iron(II) sulphate[247,267-269]. The resulting copolymers dissolve in acetone, form transparent films, and have good electrical and thermal stability[270]. The presence of hydrogen and halogen atoms enables these copolymers to be cross-linked by ethyl cyanoacetate, hexanonitrile, acetonitrile, cyanoacetic acid, acrylonitrile, cyanoacetamide, etc.[271]

Vinyl fluoride copolymerises with trifluoroethylene in the presence of inorganic and organic peroxides, di-isopropyl peroxodicarbonate, and organoboron initiators in the mass, suspension, emulsion, and solution[66,240,267,272]. These copolymers are characterised by enhanced heat resistance and are suitable for the production of films[273].

The copolymerisation of vinyl fluoride with vinylidene fluoride has been studied in greater detail[29,65,239,272-274]. The reaction is initiated by benzoyl peroxide, sodium persulphate, di-isopropyl peroxodicarbonate, organoboron catalysts—triethylboron, tributylboron tri-isopropylboron, diethylboron ethoxide, diethylboron chloride, diborane—and oxygen. The resulting copolymers are soluble, and have been used to obtain thin films and coatings[275,276]. Exposure of a mixture of vinyl and vinylidene fluorides to γ-rays (dose 7.2 rad) yields a copolymer containing 52.7% of vinyl fluoride units[277].

Vinyl fluoride copolymerises readily with perfluoromethacryloyl fluoride—a monomer that does not polymerise alone—both in the presence of chemical initiators and on exposure to γ-rays[278]. The products are partly soluble in dimethylformamide. The thermal stability of the copolymer improves with increase in the content of the acid fluoride.

Products that are thermally more stable than poly(vinyl fluoride) are obtained by copolymerising vinyl fluoride with 1,1-difluoroisobutene[273], perfluoropropene[29,240,247], 1,1,2,4-tetrafluorobuta-1,3-diene[279], 1,1,2- and 1,1,3-trifluorobuta-1-diene [sic][280], fluorinated ketones[281,282], perfluoronitroisomethane [sic][283,284], halogenotrifluorocyclopropanes[283], and dichlorodifluoroethylene[285].

Vinyl fluoride copolymerises with vinyl acetate in bulk, solution, or aqueous dispersion in the presence of benzoyl peroxide[251,254,268,286,287] or on ultraviolet irradiation[288]. At 0–80°C copolymerisation takes place readily in the presence of di-isopropyl peroxodicarbonate and organoboron initiators[195,239,247]. The products possess great resilience and resistance to sunlight[289]. Aqueous solutions of partly hydrolysed copolymers of vinyl fluoride with vinyl acetate yield thermally reversible gels[286]. Detailed studies have been made of the radiation copolymerisation of vinyl fluoride and acetate in the mass and dissolved in 1,1-dichloroethane, acetone, dimethylformamide, and several other solvents[290,291]. The rates of copolymerisation in the mass and in 1,1-dichloroethane solution are proportional to the dosage rate to the power 0.78 and 0.55 respectively. Increase in the vinyl fluoride content of the copolymer is accompanied by an increase in its density, rises in the glass and flow points, and strengthening of the films formed from it. The activation energy of the thermal degradation of poly(vinyl acetate) and of copolymers containing 14% and 35% of vinyl fluoride is respectively 32.0, 40.7, and 43.5 kcal mole^{-1}.[209]

Under the influence of γ-rays vinyl fluoride copolymerises with vinyl propionate in the mass and in 1,1-difluoroethane solution[251,254]. The product is transparent and rubberlike, softens at 140°C, and decomposes at 285°C. Vinyl fluoride has been copolymerised also with 3,5-dichloromethylstyrene[255]. The suspension copolymerisation of vinyl fluoride has been accomplished also with vinyl butyrate, benzoate, and succinate, diethyl and dibutyl maleates, and dioctyl fumarate in the presence of lauroyl peroxide[43,44,251,254]. The resulting copolymers possess enhanced resistance to heat and light with good electrical insulation.

Investigation of the copolymerisation of vinyl fluoride with acrylic and methacrylic acids and esters in the presence of free-radical initiators has established[52,239,241,292-299] that the esters are less active than are the corresponding acids. A similar rule is observed in their radiation copolymerisation[297]. The rate of copolymerisation is proportional to the dosage rate to the power 0.55 to 0.80, and increases on passing from acrylates having large groups to the acid itself. The copolymers are enriched with the acrylic monomers in all the systems studied. Copolymers of vinyl fluoride with acrylic and with methacrylic acids, whether obtained chemically or by the radiation method, do not exhibit fluidity, though the glass point falls as the vinyl fluoride content increases. The copolymers with the esters develop rubberlike elasticity, and both glass and flow points rise with increase in the vinyl fluoride content, which is attributed to the strengthening of intermolecular interaction by the presence of the polar carbon–fluorine bond. The copolymers are intermediate in thermal stability between the corresponding homopolymers of the acrylic monomer and poly(vinyl fluoride)[209].

A copolymer of vinyl fluoride with *N*-vinylpyrrolidone has been prepared by a radiation method[300]. The latter component is more reactive than the former by a factor of 63, on interaction both with its own radical and with that of vinyl fluoride. The solubility of the copolymer depends on the dosage rate and on the integral dose. Chemically prepared copolymers are completely soluble in polar solvents[301].

The copolymerisation of vinyl fluoride with acrylonitrile has been widely studied in the mass, in solution, and in suspension in the presence of benzoyl and lauroyl peroxides, di-isopropyl peroxodicarbonate, perfluoroacyls, and organoboron compounds at 0–50°C.[44,248] Water-soluble copolymers of maleic anhydride with ethylene or vinyl acetate served as dispersing agent for the suspension copolymerisation[44]. A radiation method has also been used for the copolymerisation of vinyl fluoride with acrylonitrile in the mass and in solution in benzene and dimethylformamide[256,302]. Examination of the influence of rate of irradiation on rate of copolymerisation established the same rules as for the binary systems of vinyl fluoride with vinyl chloride, vinylidene chloride, and *N*-vinylpyrrolidone. Copolymers of irregular structure are formed, but with a high content of vinyl

fluoride in the initial monomer mixture short segments comprising vinyl fluoride and acrylonitrile units alternate. The copolymers are obtained in cross-linked forms, so that they are only partly soluble; the insoluble portions of the copolymers are enriched with acrylonitrile units.

Waxlike solid copolymers of vinyl fluoride with hydrogen cyanide [303] are obtained in the presence of free-radical initiators at 135°C and 1000 atm. Copolymers of vinyl fluoride can be obtained with methylenemalononitrile, α-cyanoacrylamide, methylenemalonamide [304], and α-acetamidoacrylamide [305,306].

Several studies have been made also on ternary copolymers of vinyl fluoride. Thus readily soluble, non-flammable products are obtained by copolymerising vinyl fluoride and tetrafluoroethylene with chlorotrifluoroethylene [307], vinyl chloride, and vinylidene fluoride respectively. The ternary copolymer comprising 60% of vinyl fluoride, 25% of tetrafluoroethylene, and 15% of vinyl chloride possesses good physicochemical and adhesive properties [308]. Copolymerisation of vinyl fluoride with chlorotrifluoroethylene and vinylidene fluoride under the influence of γ-rays has been described [254]. Polymers that melt with decomposition are obtained by copolymerising vinyl fluoride with bishydroxyalkyl maleates and vinylidene halides [267]. Heat-resistant copolymers of vinyl fluorides with bicyclo-[2,2,1]hept-2-ene and *N*-carboxylated bicyclo[2,2,1]hept-2-ene derivatives have been prepared [309]. Copolymers having good cross-linking properties are obtained from vinyl fluoride with acrylates and $\alpha\beta$-alkenes [310]. Vinyl fluoride can be copolymerised with a small quantity of vinyl acetate and itaconic acid or with maleic anhydride and isobutyl vinyl ether to improve the dyeing properties of poly(vinyl fluoride) fibres [309]. A copolymer of high adhesive power, soluble in cheap solvents, is obtained from vinyl fluoride with vinyl benzoate, bis-2-chloroethyl vinylphosphonate, itaconic acid, and tetrafluoroethylene [311]; the product melts at 182°C.

Radiation copolymerisation of equimolecular ternary mixtures of vinyl fluoride and vinyl acetate with vinyl chloride and with methyl methacrylate respectively has been studied in the greatest detail [312-316] with the use of cobalt-60 γ-rays at dosage rates of 16, 70, and 100 rad s^{-1} for various lengths of time. The order of reaction with respect to the dosage rate is respectively 0.74 and 0.64 for the two ternary systems. Copolymers obtained in the initial stages are in all cases enriched with the more active monomers—vinyl acetate with vinyl chloride and methyl methacrylate respectively—but as they are consumed the content of vinyl fluoride in the monomer mixture increases, with a consequent increase in its content in the copolymer also. The infrared spectrum [315,316] of the ternary copolymer of vinyl fluoride with vinyl chloride and acetate shows a sharp drop in intensity of carbon–chlorine stretching vibrations in comparison with the spectrum of the binary copolymer of the latter components. Furthermore, bands in the range 1000 to 1200 cm^{-1} are broadened by the presence of bands due to stretching vibrations of ester carbon–oxygen–carbon bonds and of carbon–fluorine bonds. The nuclear magnetic resonance spectrum [315,316] of this copolymer contains three groups of signals, in the ranges 1.7–2.5, 4.0–4.7, and 4.9–6.5 ppm: the sharp peak at 2.0–2.05 ppm corresponds to methoxy-groups in vinyl-acetate segments; and the signal in the range 4.0–5.5 ppm is due to the superposition of signals of tertiary protons in fluoromethylene, chloromethylene, and acetoxymethylene groups. The ternary copolymers of vinyl fluoride and acetate with vinyl chloride and with methyl methacrylate respectively have lower glass points than have the corresponding binary copolymers, and these fall with increase in the vinyl fluoride content of the copolymer [314].

V. GRAFT POLYMERISATION OF VINYL FLUORIDE

At the end of the 1960s, when the valuable properties of poly(vinyl fluoride) had become clear, intensive study began both of the preparation and of the properties of graft copolymers based on vinyl fluoride [317,318]. The low boiling point, resistance to polymerisation in the presence of material initiators, and inertness towards most polymers hinder considerably the graft polymerisation of vinyl fluoride by chemical and mechanochemical methods. The most effective has proved to be the radiation method, by which has now been accomplished the graft polymerisation of vinyl fluoride to cellulose and its derivatives, natural silk, wool, kapron fibre, polyalkenes, and halogenated and several other polymers [98,113,319-340].

The radiation graft polymerisation of vinyl fluoride to cotton cellulose and cellulose hydrate has been conducted in the mass in the presence of dimethylformamide, ethanol, and water [325,326]. With increase in the time of irradiation both the overall conversion of vinyl fluoride and the yield of the graft copolymer increase.

Graft polymerisation of vinyl fluoride from the vapour phase goes best on mercerised and "inclusion" cellulose [326]. This is due to enhancement of the reactivity of cellulose by the loosening of its structure during mercerisation and inclusion. The increase in weight due to the grafted poly(vinyl fluoride) is larger in the presence of the vapours of such "including" substances as dimethylformamide or isopentanol than on an already "included" specimen. The larger gain in the first case is due to the grafting of vinyl fluoride at the instant at which the cellulose swells.

The grafting of poly(vinyl fluoride) to cotton cellulose weakens the infrared absorption band in the range 1325 to 1350 cm^{-1}, due to deformation vibrations of primary hydroxy-groups [330]. This indicates that active grafting centres are located at these groups. The band in the region of 900 cm^{-1} also diminishes in intensity, which is attributed to loosening of the structure of compact segments of cellulose under the influence of the grafted poly(vinyl fluoride) chains.

The infrared spectra of cellulose hydrate [330] exhibit the same changes as in cotton cellulose, but the weakening of vibrations in the range 3200–3300 cm^{-1} is most clearly evident. Absorption diminishes also in the range 1000 to 1020 cm^{-1}, which suggests that active centres may well be formed not only at primary but also at secondary hydroxy-groups. Modified cellulose hydrate containing 8% of poly(vinyl fluoride) resists the action of sulphuric acid for 1 month, whereas an unmodified specimen breaks down completely within a few minutes. Increase in the content of the grafted polymer diminishes the sorption of water vapour, which is attributed to the strongly hydrophobic character of the poly(vinyl fluoride) side-chains.

Study of the thermal stability of graft copolymers of cotton cellulose with poly(vinyl fluoride) in a vacuum and in air over the temperature range 270–370°C has established [333] that the initial rates of decomposition of the copolymers are considerably lower than those of the initial cellulose.

The graft polymerisation of vinyl fluoride on cellulose triacetate fibre is more rapid than on the diacetate [327], which is due to the greater radiation sensitivity of the

former. Graft copolymers of the diacetate and the triacetate containing >40% of poly(vinyl fluoride) dissolve neither in acetone nor in chloroform, and undergo partial swelling in dimethylformamide and cyclohexanone.

Graft polymerisation of vinyl fluoride to natural silk does not take place in the absence of solvents [331]. The presence of such liquids as water, methanol, and ethanol has a sensitising effect on grafting, and the increase in weight reaches 20% on the weight of the silk. The grafting of vinyl fluoride effects a marked improvement in the acid resistance of natural silk, which is attributed to shielding of the peptide links by the grafted polymer chains [332,333]. Furthermore, grafting improves the resistance of silk to heat and light, as well as its oil- and water-repellent properties. Electron microscopy has established that the grafting of vinyl fluoride to natural silk diminishes the fibrillarity characteristic of the original fibre [335,341]. Individual globular structures are also observed, whose presence is due to the grafted chains of lyophobic poly(vinyl fluoride).

Vinyl fluoride has been grafted from the vapour phase to kapron fibre at dosage rates of 12–100 rad s^{-1}, [113,317,323] when the resulting copolymers contain up to 31% of the grafted polymer. In the presence of water vapour the gain in weight increases to 60%. [336] This may be due to the great swelling of kapron fibre in water vapour and to the sensitising action of radicals formed in the radiolysis of water. The yield of graft copolymer is lower in the presence than in the absence of methanol and ethanol vapours. Grafting is influenced also by the fibre structure [336]: the gain in weight is larger on an unoriented than on an oriented fibre and a tyre cord. The grafting of vinyl fluoride enhances the light, heat, and chemical resistance of kapron [113].

Radiation vapour-phase grafting of vinyl fluoride has been accomplished also on natural wool [333]. Grafting is greatest in the presence of water vapour. At 90°C modified wool containing 10% of a poly(vinyl fluoride) graft dissolves more slowly than unmodified wool in caustic soda by a factor of almost 400.

Detailed studies have been made on the radiation graft polymerisation of vinyl fluoride to polyethylene, polypropylene, and polyisobutylene. Vinyl fluoride has been grafted to polyethylene (in film or powder form) from the vapour phase at 38°C and 27.5 atm [98,113] with dosage rates varying from 10 to 100 rad s^{-1}. The radiation-chemical yield fluctuates within the range 100–3800 mol./100 eV in the case of a film, and 870–9540 mol./100 eV for a powder. A graft copolymer containing <30% of poly(vinyl fluoride) is completely soluble in boiling toluene and in xylene [113]. With further increase in the content of the graft the solubility diminishes, and a gel is formed consisting of a graft copolymer of polyethylene containing very long poly(vinyl fluoride) side-chains. The grafting of vinyl fluoride increases the density of polyethylene to 1.082 g cm^{-3} for a copolymer containing 50.2% of poly(vinyl fluoride). The splitting of the absorption band due to vibrations of the methylene group in the region of 720 and 730 cm^{-1} in the infrared spectra of the copolymer [98] gradually disappears with increase in the poly(vinyl fluoride) content. This shows that grafting takes place both in amorphous and in crystalline regions of polyethylene, and leads to breakdown of the crystal structure of the latter. In graft copolymers containing ≥25% of poly(vinyl fluoride) fluidity is completely absent owing to cross-linking of the side-chains of the latter by the elimination of hydrogen fluoride under the influence of temperature [98].

As with polyethylene the modification of polypropylene by the grafting of vinyl fluoride increases its density while diminishing its solubility and swellability [329]. Graft copolymers of polyisobutylene with vinyl fluoride has been prepared in cyclohexanone with equimolecular proportions of polymer, monomer, and solvent and dosage rates of 9–126 rad s^{-1}. [338] As in the other cases, the poly(vinyl fluoride) content of the copolymer increases with the dose whatever the dosage rate. This is accompanied by increase in the heat and chemical resistance of the copolymer.

Vinyl fluoride has been grafted to polytetrafluoroethylene with the aim of improving the adhesive properties and diminishing the cold flow of the latter [338]. When polytetrafluoroethylene is irradiated in liquid vinyl fluoride, the homopolymer is formed preferentially. Better results are obtained by conducting the graft copolymerisation from the vapour phase. The resulting graft copolymers are readily wetted by polar liquids while retaining all the valuable properties of the original polytetrafluoroethylene.

Radiation grafting to poly(vinyl chloride) has been accomplished both in pure vinyl fluoride vapour and in the presence of vapours of various solvents [338–340], among which the presence of 1,1-dichloroethane gave the largest degree of grafting. With increase in the poly(vinyl fluoride) content of the copolymer from 6.7% to 35.8% the loss in weight in a vacuum and in air decreases by factors of 1.5–4, and 1.5–6 respectively [342]. Vinyl fluoride has been grafted also on khlorin fibre, obtained from chlorinated poly(vinyl chloride) [113,317,343]. The rate of the graft copolymerisation is proportional to the dosage rate to the power 0.61. Improvement in the heat, light, and chemical resistance of khlorin is noted.

Vinyl fluoride has been grafted on polystyrene [338], polyvinyl alcohol [98,113], poly(vinyl acetate) [98,338,340], and poly(methyl methacrylate) [98,337,338]. With polystyrene dosage rates of 9–126 rad s^{-1} were used in 1,1-dichloroethane and chloroform. Increase in the poly(vinyl fluoride) content of the copolymer was accompanied by decrease in its swellability in toluene and fall in its glass point. A copolymer containing 5.6% of grafted poly(vinyl fluoride) decomposes at little more than one-sixth of the rate of decomposition of the original polystyrene.

Under identical conditions vinyl fluoride can be grafted considerably more rapidly to kapron than to polyvinyl alcohol [98,113]. This is explained by the low activity of the macroradical from the polymeric alcohol and by the formation of a very compact, oriented jacket on the surface of the fibre during its formation. Fluidity is completely absent from graft copolymers containing 28% of poly(vinyl fluoride), as from graft copolymers of polyethylene, owing to cross-linking at the time of the thermal test.

The radiation grafting of vinyl fluoride on poly(methyl methacrylate) has been accomplished in benzene and in 1,1-dichloroethane [98,338]. The glass points of the resulting graft copolymers were lower than that of the original methacrylate polymer, which is attributed to the plasticising action of the grafted chains. The grafting of vinyl fluoride on poly(vinyl acetate) strongly enhances the resistance of the latter to organic solvents and mineral acids [338], as well as raising the flow point. Thus graft copolymers containing 11.2% and 59.0% of poly(vinyl fluoride) have flow points of 116 and 198°C respectively.

Although poly(vinyl fluoride) has relatively good adhesive properties among fluorinated polymers, and can be dyed and processed comparatively readily, further improvement in these properties is of great practical interest. For this purpose styrene [343–346], methyl meth-

acrylate [344,346,347], vinyl acetate [346,347], and vinylidene chloride [344] have been grafted on a poly(vinyl fluoride) film, both under the influence of cobalt-60 γ-rays and by the use of an electron accelerator, and methyl methacrylate has been grafted on a copolymer of trifluoroethylene and vinyl fluoride under the influence of ultrasound [345]. Among these monomers methyl methacrylate gave the best graft [346], because of its high radiation sensitivity: almost all the methyl methacrylate was grafted during the first hour of irradiation. In the case of styrene the rate of grafting passes through a maximum with increasing time of exposure [343], which is attributed to the shielding effect of the more radiation-resistant grafted polystyrene.

These monomers form the sequence

vinyl acetate < styrene < methyl methacrylate

of increasing rate of grafting to poly(vinyl fluoride), which correlates with their sorption on the polymer [346]. The graft layer formed initially has a significant influence on the subsequent course of the process. Grafting obviously loosens the film surface, which facilitates diffusion of the monomers into the interior. Loosening of the structure of poly(vinyl fluoride) by grafting has been confirmed by X-ray diffraction and by a study of the density of graft copolymers [346,348].

The thermomechanical curves of graft copolymers containing up to 30% of methyl methacrylate or styrene are analogous to those of the original poly(vinyl fluoride) [346,347]. With further increase in the content of the grafted component segments appear in the curve corresponding to a vitreous state, rubberlike elasticity, and viscous flow.

Grafting the above monomers improves the wettability and dyeing properties of a poly(vinyl fluoride) film [346-348]. This effect is due firstly to the appearance on the film surface of functional groups that increase its affinity for liquids and secondly to diminished crystallinity of the polymer. With the same content of the grafted polymer the wettability by water increases in the sequence

poly(methyl methacrylate) < polystyrene < poly(vinyl acetate).

The increased adhesive power of modified poly(vinyl fluoride) is due [346] to the presence of the grafted side-chains, not to any other factor, in particular not to the influence of the γ-rays. The dyeability of the graft copolymers of poly(vinyl fluoride) increases in the sequence [348]

polystyrene < poly(methyl methacrylate) < poly(vinyl acetate).

This rule is due to the nature of the grafted polymers, since under identical conditions the dyeability of the polymers themselves also increases in the same sequence.

VI. PROCESSING AND APPLICATION OF VINYL FLUORIDE POLYMERS

Poly(vinyl fluoride) can be processed into appropriate articles by all the methods that have been developed for and applied to other thermoplastic polymers, although its characteristic features must be taken into account. Injection moulding of poly(vinyl fluoride) above 200°C was suggested [12] for the production of films or monolithic articles possessing good impact strength. The possibility of film formation from solution was also examined [12]. A dimethylformamide solution containing 8% of the polymers was quite adequate for this purpose, and film formation was hindered from higher solution concentrations. However, the only method that found wide application for the production of poly(vinyl fluoride) films was extrusion. Various stabilisers must then be used to prevent thermal degradation [218,349].

The most convenient method has proved to be moulding in the presence of so called latent solvents, which tend to lower the melting point and diminish orientational stretching of the polymers, thereby preventing degradation [350]. Latent solvents, by causing partial dissolution and good swelling, promote high dispersion of the polymer. Homogeneous films containing up to 50% of poly(vinyl fluoride) have been prepared from such fine dispersions [81,93,351-357]. The latent solvent most often employed is dimethyl sulphoxide, either alone [350,358-360] or in the presence of an electroluminescent substance. Various lactones [351,353,361], tetramethylurea, triethyl phosphate [78], pyrrolidones [93], and piperidines [362,363] have also been proposed as latent solvents.

A method has been suggested for the production of both films and fibres from aqueous dispersions of poly(vinyl fluoride) in the presence of small quantities of a latent solvent [78,364,365]. Mixtures of water and sulpholan have also been proposed as dispersion medium [356]. The role of the latent solvent is aggregation of particles; although aggregates are formed from the accumulation of a few particles, they are separated from one another by a thin layer of solvent.

The processing of poly(vinyl fluoride) into films can be facilitated by preparing dispersions during the actual synthesis of the polymer in the presence of latent solvents. This avoids isolation and redissolution or redispersion of the polymer. Thus a film prepared from a 22% dispersion of poly(vinyl fluoride) synthesised in a medium containing 71% of dimethyl sulphoxide and 7% of water has good mechanical properties [366]. Opaque films devoid of lustre can be obtained by introducing into the dispersion an opalescent substance such as titania [367] or silica [368]. Various pigments, stabilisers, and plasticisers are also used in the preparation of poly(vinyl fluoride) films [152,369-377].

Several difficulties are involved in orienting the films at low temperatures: in all cases local stretching occurs, leading to non-uniformity of thickness over the area of the film [152]. These difficulties can be avoided by orienting films containing at least 35% of a latent solvent [377]. In this way a film 1.04 mm thick has been obtained from a sheet of poly(vinyl fluoride) 13.9 mm thick. At the present time films of this polymer are produced only in the USA, under the name Tedlar [378]. Several brands are available, differing in tensile strength—from the high value of 1265 kgf cm^{-2} with great bending strength to the low value of 492 kgf cm^{-2}.

During recent years the possibility of obtaining fibres from poly(vinyl fluoride) has also been studied. Thus Knunyants et al. [379] developed methods for obtaining a technical fibre from the bulk polymer. A fibre can be prepared from the paste obtained by drying an emulsion of the polymer stabilised with partly hydrolysed adiponitrile [380], which acts also as a plasticiser. Monofilaments of tenacity 5 g denier^{-1} can be formed from the polymer of reduced viscosity 1.25, by extruding a coalescing dispersion into a latent solvent [381].

The use of poly(vinyl fluoride) in coatings has proved especially fertile. They are distinguished by high adhesion, resistance to chemical reagents, abrasion, and weathering, and a wide range of working temperatures. The polymer composition for their production is prepared

by methods that are widely employed in the paint and varnish industry [350,382,383]. It contains not only the polymer and solvents but also pigments, stabilisers, fillers, and modifiers [180,350,384,385]. Pigments are selected on the basis of their thermal stability during baking and their behaviour in the final coating [350]. Various fillers, e.g. calcium silicate, magnesium silicate, and silicon dioxide, are also used [350].

Various viscosity modifiers are necessary ingredients in obtaining polymer coatings [350]. They should be soluble in an inert solvent and thermostable, and should neither prevent adhesion nor exert an adverse influence on the properties of the coating. Various acrylate polymers and poly(vinyl acetate) are generally used as modifiers [385]. In isolated cases the dispersion obtained during emulsion polymerisation can be used directly to obtain coatings [386]. A properly prepared and applied dispersion of poly(vinyl fluoride displays excellent adhesion to metals, without the need to use an organic primer. The dispersions are applied with spraying equipment, by means of reversing rollers, by dipping, and by centrifugal casting [350]. Procedures have been suggested for applying the powdered polymers in a stream of gas flowing at 100 m s^{-1}. [387]

Various compositions have now been developed for definite fields of application—to obtain transparent protective coatings, chemically stable and corrosion-resistant pigmented coatings and linings, pigmented architectural claddings [350]. In agriculture poly(vinyl fluoride) films can successfully replace those of the chloride and polyethylene for covering hotbeds and for protecting plantings from early spring frosts [388].

Poly(vinyl fluoride) can be widely applied in the building industry [165,168,350]. Panels coated with the polymer are used as external and internal facings in residential and industrial buildings [389,390]. Films of the polymer are used also for coating ornamental laminated plastics [391-399], asbestos goods [400], rolls of aluminium foil [401], charts, dials, signs and other decorative items, window and door fittings, and furniture upholstery. The useful life of such a coating functioning in the open air exceeds 25 years.

A film of poly(vinyl fluoride) in combination with polystyrene is used in the construction of luminous panels [402]. If a poly(vinyl fluoride) film 0.025 mm thick is attached to the inner surface of luminous polystyrene panels, they will function for at least 20 years.

A new brand of poly(vinyl fluoride) Delvar is also widely used for coating various articles, including those used in the building industry [403]. It is a component of the chemically resistant coating Delbon, which is unlike Tedlar film in being applied to a surface without a priming or an adhesive. Veneers having coloured poly(vinyl fluoride) coatings are manufactured under the name Welwood PF-L, [404-406] and asbestos-cement panels under the names Colorbest and Ternol [407]. Because of its great chemical resistance this polymer is used also to protect various cement structures from leaching, marine salts, and water vapour [408].

The good dielectric properties and retention of flexibility at low temperatures are recommendations for the use of poly(vinyl fluoride) film in the manufacture of electric batteries intended to function at low temperatures [409]. A more thermostable polymer, partly dehydrofluorinated and containing 26–38 wt.% of fluorine, is used as an insulator to separate two electrodes, acting as a capacitor [410]. Copolymers of vinyl fluoride with alkyl vinyl ethers have also proved suitable for this purpose [411]. Poly(vinyl fluoride) has been used in making the diphragms of electrolytic cells for the manufacture of chlorine [412].

Poly(vinyl fluoride) is used in the automobile and shipbuilding industries for coating various copper, brass, steel, and aluminium articles [166,350,413-418]. It provides excellent protection from corrosion and does not affect the decorative effect of the main material. During recent years coatings based on the polymer and on various copolymers of vinyl fluoride have come to be widely used in the container industry, instrument-making [350], and solar energy equipment [419], as well as for infrared detectors [420].

Among various fluorinated polymers poly(vinyl fluoride) exhibits relatively high radiation resistance [421]. It has therefore found application in nuclear technology [422,423] and is used as a coating for the protection of spacecraft [350,382,424]. Another reason for its use in space technology is that its loss in weight is only 0.5% under a residual pressure of around 10^{-6} mmHg at ~150°C, while articles made of it retain their appearance and shape [425,426].

The small water adsorption and high elasticity have made possible the use of vinyl fluoride polymers and copolymers for the production of photographic films [427,428]. Chemical industry is a promising field for application of the polymer, which can be used to cover and line tubes, extractor fans, reservoirs for fresh and salt water, reaction vessels, drying units, etc. [429-431] Poly(vinyl fluoride) also provides a coating for external and internal surfaces of chemical plant to prevent corrosion by chlorine, hydrochloric acid, caustic soda, acetone, petrol, tetrachloromethane, and butan-2-one [350,432].

Poly(vinyl fluoride) and various copolymers especially modified with ultraviolet absorbers are widely used for coating polyethylene [148] and poly(ethylene terephthalate) [433] films, polychloroprene felt [282,377,434], wood, and textiles [49]; they are used also as lubricants and impregnants [435].

It is thus obvious that vinyl fluoride polymers are worthy of comprehensive examination as materials having an extremely wide range of application.

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