LIBRARY

U.D.C. 541.64:547.412

Polycondensation Reactions of Fluorinated Organic Compounds

R.M.Gitina, E.L.Zaitseva, and A.Ya.Yakubovich (deceased)

The review deals with the principal advances in the synthesis and investigation of the properties of polycondensation of fluoro-polymers. In many cases the properties of the fluoro-polymers have been compared with those of their non-fluorinated analogues. The applications of the polymers are also described briefly.
The bibliography includes 138 references.

CONTENTS

I. Introduction 679
II. Fluorine-containing polyesters and polythioesters 679
III. Fluorine-containing polyamide polymers 684
IV. Fluorine-containing polyazoles 689
V. Fluorine-containing polyphenylene polymers 693

I. INTRODUCTION

The study of organofluorine polymers and low-molecular-weight compounds of this class began to develop comparatively recently—during the 1940's. The scope of the chemistry of fluorinated macromolecular compounds was of course limited mainly by the relatively low level of development of the chemistry of fluorinated low-molecular-weight compounds. This was responsible for the fact that until recently (until the 1950's) the principal methods for the synthesis of fluoro-polymers consisted in the polymerisation of the relatively readily available fluorinated olefins, which yielded polyperfluoroalkylenes. Polymerisation fluoro-polymers, particularly polytetrafluoroethylene (Teflon), which is the most important member of this class, have found a firm place among modern polymeric materials employed under severe operating conditions.

By virtue of the considerable advances in organofluorine chemistry in recent years, many aspects of this field, which were either impossible or difficult to achieve, have become more or less commonplace, in particular methods for the synthesis and the study of the properties or organic perfluoro-compounds and polyfluorinated compounds with a wide variety of functional groups have been developed on a large scale [1]. This led to the expansion of studies on the synthesis and properties of fluorinated polymers obtained by methods for the polycondensation of bi- and poly-functional monomers. The application of the polycondensation methods of synthesis to fluoro-polymers led to a much greater variety of the structures of macromolecules and thus to the development of new essential materials.

Much attention has been devoted to problems of the synthesis of polymerisation fluoro-polymers, their properties, and applications; the present review gives the first systematic account of polycondensation fluoro-polymers. It covers the original literature (including patents) up to the end of 1969 and deals with fundamental work on the synthesis and properties of polycondensation fluoro-polymers containing fluorine atoms in the main macromolecular chain and those obtained on the basis of bifunctional derivatives of 2,2-diphenylperfluoropropane.

II. FLUORINE-CONTAINING POLYESTERS AND POLYTHIOESTERS

Fluorine-containing polyethers are mainly obtained by the polymerisation of epoxyfluoroalkanes. In contrast, polyesters are synthesised by the polycondensation method.

The first fluorine-containing aliphatic polyesters were described in 1952. [2] At the present time fluorine-containing aliphatic, alkylene, aromatic, and fully aromatic polyesters are known. Depending on which component contains fluorine, polyesters can be divided into two types: (1) polyesters from fluorinated dicarboxylic acids and non-fluorinated diols; (2) polyesters from fluorinated dicarboxylic acids and fluorinated diols; (3) polyesters from non-fluorinated dicarboxylic acids and fluorinated diols. Table 1 lists the fluorine-containing polyesters described in the literature and some of their properties.

Aliphatic polyesters of the first type were obtained by the direct esterification of glycols by perfluoroalkanedicarboxylic acids [2,3]:

$$HO(CH_2)_m OH + HOOC(CF_2)_p COOH \xrightarrow{-H_2O} [-O(CH_2)_m OCO(CF_2)_p CO-]_n,$$

and also by the reaction of the silver salts of these acids with $\alpha\omega$-di-iodoalkanes [3]. The polyesters synthesised by the second method have lower viscosities than those obtained by direct esterification.

Data have also been published on the synthesis of fluorine-containing polythioesters by the reaction of pentane-1,5-dithiol and perfluoroglutaric acid dianhydride [4] and also by the reaction of hexane-1,6-dithiol with polyfluorochlorohexanedicarboxylic acid [5]. Aliphatic polyesters of the second type can be obtained by the reaction with tetrahydroperfluoroalkane-$\alpha\omega$-diols of both perfluoroalkanedicarboxylic acids in the presence of zinc chloride as a catalyst [6,7] and their dianhydrides [8]; however, these polyesters have a low molecular weight. Polyesters with a high molecular weight can be obtained using acid dichlorides [6,7], since fluorinated diols are acidic compounds and are esterified with difficulty.

It is noteworthy that polyesters obtained from perfluoroalkanedicarboxylic acids are hydrolysed much faster than their non-fluorinated analogues [3,8] and therefore they have not found practical applications [7]. The enhanced

Table 1. Fluorine-containing polyesters and polythioesters.

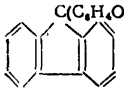
Initial components		Certain properties of polymers	References
glycols, iodides, and thioglycols	acids and their derivatives		
$(CH_2)_2(OH)_2$	$(CF_2)_4(COOH)_2$	Waxy substance T_f = 129–133°C; insol. in hydrocarbons and usual organic solvents	2
$(CH_2)_4(OH)_2$	$(CF_2)_3(COOH)_2$	Viscous oil	3
$(CH_2)_3I_2$	$(CF_2)_3(COOAg)_2$	ditto	3
$(CH_2)_3I_2$	$(CF_2)_3(COOAg)_2$	,,	3
$(CH_2)_2(OH)_2$	$C_6F_4(COOCH_3\text{-}p)_2$		35
$(CH_2)_5(SH)_2$	$CF_2(CF_2CO)_2O$	Waxy substance, insol. in usual organic solvents	4
$(CH_2)_6(SH)_2$	$(CF_2CFCl)_4(COOH)_2$	Solid substance, insol. in ααα-trifluorotoluene	5
$C(CH_3)_2(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	η_{inh} = 0.4, (Ref.8) T_{soft} = 290°C; polymer soluble in many organic solvents; strong sheet formed from solutions	27, 28
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	η_{inh} = 0.66, T_{soft} = 340°C; polymer soluble in many organic solvents; strong sheets formed from solutions	27, 28
$C(CH_3)_2(C_6H_4OH\text{-}p)_2$	$i\text{-}C_6F_4(COCl)_2$	$\eta_{inh} \simeq 0.1$	36
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(COOH)_2$	$M \simeq 8000\text{–}9000$, T_{degr} = 380°C	6,7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(COCl)_2$		7,18
$(CF_2)_3(CH_2OH)_2$	$CF_2(CF_2CO)_2O$		8
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_4(COOH)_2$	Viscous liquid, slowly crystallising	6,7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_4(COCl)_2$	M = 6570, $T_{brittle}$ = –55°C, T_f = 35°C	6,7
$(CF_2)_3(CH_2OH)_2$	$C_7F_{15}CF(CF_2COCl)_2$	M = 9920	7
$(CF_2)_3(CH_2OH)_2$	$C_3F_7CH(CH_2COCl)_2$	Viscous liquid, M = 7200, $T_{brittle}$ = –25°–30°C	6,7
$(CF_2)_3(CH_2OH)_2$	$S[CH(C_3F_7)CH_2COCl]_2$	M = 7480	7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(CH_2OCH_2COCl)_2$	M = 5360	7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(C_6H_4COCl\text{-}m)_2$	T_g = 16°C, T_{soft} = 20°C, T_f = 147°C	33
$(CF_2)_5(CH_2OH)_2$	$(CF_2)_5(C_6H_4COCl\text{-}m)_2$	T_g = 16°C, T_{soft} = 20°C, T_f = 125°C	33
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(COOH)_2$		6,7
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(COCl)_2$	$M \simeq 8800\text{–}9900$	7
$(CF_2)_4(CH_2OH)_2$	$CF_2(CF_2CO)_2O$		8
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_4(COCl)_2$	Waxy substances, M = 5260, T_f = 65–70°C	6,7
$(CF_2)_4(CH_2OH)_2$	$C_7F_{15}CF(CF_2COCl)_2$	M = 10400	7
$(CF_2)_4(CH_2OH)_2$	$C_3F_7CH(CH_2COCl)_2$	M = 9940	7
$(CF_2)_4(CH_2OH)_2$	$S[CH(C_3F_7)CH_2COCl]_2$	M = 7400	7
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(CH_2OCH_2COCl)_2$	M = 6850	7
$(CF_2)_3(C_6H_4OH\text{-}m)_2$	$(CF_2)_3(C_6H_4COCl\text{-}m)_2$	T_g = 46°C	33
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(CF_2)_4(COCl)_2$	η_{log} = 0.30, T_{soft} = 120°C, sol. in tetrachloroethane, amorph.	26
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(CF_2)_6(COCl)_2$	η_{log} = 0.40, T_{soft} = 80°C, sol. in tetrachloroethane	26

Table 1 cont'd

Initial components: glycols, iodides, and thioglycols	Initial components: acids and their derivatives	Certain properties of polymers	References
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.5$, $T_{soft} = 280°C$; polymer sol. in many organic solvents, strong sheets formed from solutions	27, 28
$C_6H_5C(CF_3)(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.72$, $T_{soft} = 300°C$, strong sheets formed from solution	27, 28
$(C_6F_4OH\text{-}p)_2$	$m\text{-}C_6F_4(COCl)_2$	$T_{soft} = 300°C$, $T_f > 400°C$	34
$(C_6F_4OH\text{-}p)_2$	$p\text{-}C_6F_4(COCl)_2$		34
$(C_6F_4OH\text{-}p)_2$	$m\text{-}C_6F_4(OCOCl)_2$		36
$C_6F_4(OH\text{-}m)_2$	$m\text{-}C_6F_4(OCOCl)_2$	$\eta_{inh} = 0.04\text{-}0.1$	36
$C_6F_4(OH\text{-}m)_2$	$CO(OC_6H_5)_2$		36
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_3(COCl)_2$	Waxy substance; $M = 6020\text{-}7930$, $T_{brittle} = -50\text{-}-55°C$, $T_f = 40°C$	6, 10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_4(COOH)_2$	Viscous liquid, crystallising slowly; $M = 9000$	6
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Rubberlike substance, crystallising slowly; $M = 20000\text{-}25000$, $T_{brittle} = 65°C$, $T_g = 57°C$, $T_f = 30°C$, $T_{decomp} = 380°C$ (helium)	6, 10, 12, 14, 16, 18
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_6(COCl)_2$	$M = 7480$, $T_{brittle} = -75°C$, $T_f = 20\text{-}26°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_7(COCl)_2$	$M = 12000$, $T_f = 30°C$, $T_{brittle} = -48\text{-}65°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_8(COCl)_2$	$M = 11000$, $T_f = 30°C$, $T_{brittle} < -65°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2SCH_2COOH)_2$	Rubberlike substance; $T_{brittle} = -40°C$	6
$(CF_2)_3(CH_2OH)_2$	$(CH_2SCH_2COOC_2H_5)_2$		10
$(CF_2)_3(CH_2OH)_2$	$CH_2(SCH_2COOH)_2$	Waxy substance; $T_f = 55°C$	6
$(CF_2)_3(CH_2OH)_2$	$p\text{-}C_6H_4(COCl)_2$	Solid sol. in acetone, ethyl acetate, and methylene chloride; $T_f = 107°C$	13, 19
$(CF_2)_3(CH_2OH)_2$	$m\text{-}C_6H_4(COCl)_2$	Transparent pale-brown solid; films and fibres formed from the melt; $\eta_{inh} = 0.16$, $T_g = 22°C$, $T_{decomp} = 460\text{-}480°C$ (nitrogen, helium)	12, 18
$(CF_2)_4(CH_2OH)_2$	$1,3,5\text{-}(COOH)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark solid partly sol. in DMFA	20
$(CF_2)_4(CH_2OH)_2$	$1,3,5\text{-}(COCl)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark rubberlike substance sol. in DMFA; $\eta_{inh} = 0.18$, $T_{decomp} = 440°C$, $T_g = -30°C$	20
$(CF_2)_4(CH_2OH)_2$	$1,3,5\text{-}(COOC_2H_5)_2(n\text{-}C_5H_{11}O)C_6H_3$	$\eta_{inh} = 0.28$, $T_{decomp} = 445°C$ (nitrogen)	20
$(CF_2)_4(CH_2OH)_2$	$1,3,4\text{-}(COOCH_3)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark rubberlike substance; $\eta_{inh} = 0.25$, $T_{decomp} = 410°C$, $T_g = 9°C$	20

Table 1 cont'd

Initial components: glycols, iodides, and thioglycols	Initial components: acids and their derivatives	Certain properties of polymers	References
$(CF_2)_3(CH_2OH)_2$	1,3,2-$(COOCH_3)_2$ $(n\text{-}C_5H_{11}O)C_6H_2$	Dark rubberlike substance; $\eta_{inh} = 0.12$, $T_{decomp} = 400°C$, $T_g = 17°C$	20
$(CF_2)_3(CH_2OH)_2$	$o\text{-}C_6H_4(COCl)_2$	$T_{decomp} = 480°C$ (helium); sheets and fibres formed from the melt	12, 18
$(CF_2)_3(CH_2OH)_2$	$o\text{-}C_6H_4(COCl)_2$	$T_{decomp} = 480°C$ (helium)	18
$(CF_2)_3(CH_2OH)_2$	$(C_6H_4COCl\text{-}o)_2$	$T_g = 45°C$, $T_{soft} = 50°C$, $T_f = 145°C$	33
$(CF_2)_3(CH_2OH)_2$	$O(C_6H_4COCl\text{-}p)_2$	$T_{decomp} = 500°-520°C$ (helium); sheets formed from the melt	18
$(CF_2)_3(CH_2OH)_2$	$O(C_6H_4COCl\text{-}m)_2$	$T_g = 20°C$, $T_{soft} = 28°C$, $T_g = 115°C$	33
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_5(OC_6H_4COCl)_2$	$T_{decomp} = 480°C$ (helium)	18
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_3(COCl)_2$	Waxy substance, $M = 6600$-8950, $T_{brittle} = -50$-$55°C$, $T_f = 40°C$	6,10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Waxy substance; $M = 18300$-24000, $T_f = 60$-$70°C$	6,10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_6(COCl)_2$	$M = 8800$, $T_f = 58$-$61°C$	10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_7(COCl)_2$	$M = 13000$, $T_f = 47$-$50°C$	10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_8(COCl)_2$	$M = 65800$, $T_f = 55$-$60°C$	10
$(CF_2)_4(CH_2OH)_2$	$C_3H_7CH(CH_2COCl)_2$	Viscous liquid; $M = 8770$, $T_{brittle} = -25°C$	6
$(CF_2)_4(CH_2OH)_2$	$(CH_2SCH_2COOH)_2$	Rubberlike substance; $T_{brittle} = -38°C$	6
$(CF_2)_4(CH_2OH)_2$	$CH_2(SCH_2COOH)_2$	Waxy substance; $T_f = 70$-$75°C$	6
$m\text{-}(CF_2)_5(CH_2OH)_2$	$m\text{-}C_6H_4(COOH)_2$		19
$(CF_2)_5(CH_2OH)_2$	$m\text{-}C_6H_4(COOCH_3)_2$		19
$O(CF_2CF_2CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Viscous liquid $M = 16700$, $T_{brittle} = -58°C$	11
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	$T_{soft} = 340°C$; slightly sol. in chloroform and cresol; cryst.	22, 23, 26
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.60$, $T_{soft} = 240°C$; sol. in chloroform and cresol; cryst.; forms strong sheets	23
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(C_6H_4COCl\text{-}p)_2$	$T_{soft} = 400°C$; slightly sol. in chloroform and 3:1 tetrachloroethane-phenol mixt.	25
$(CF_3C(C_6H_5)(C_6H_4OH\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.60$, $T_{soft} = 290°C$; sol. in chloroform and cresol; amorph.; forms strong sheets	23, 26
$(CF_3C(C_6H_5)(C_6H_4OH\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.64$, $T_{soft} = 260°C$; sol. in chloroform and cresol; amorph.; forms strong sheets	23, 26
$(CF_2)_3(CH_2OH)_2$	$COCl_2$	Waxy substance; $\eta_{inh} = 0.30$, $T_f = 58$-$60°C$, $T_{decomp} = 450°C$ (air, helium); cryst.	18, 21
$(CF_2)_3(C_6H_4OH\text{-}m)_2$	$COCl_2$	$T_g = 71°C$	33

Table 1 cont'd

Initial components		Certain properties of polymers	References
glycols, iodides, and thioglycols	acids and their derivatives		
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$COCl_2$	$M = 25000$, $T_{soft} = 164°C$	22, 30
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$CO(OC_6H_5)_2$	Sol. in acetone	30
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$CSCl_2$	$M = 12000$, $T_{soft} = 161°C$, $T_f = 215\text{-}220°C$; sol. in carbon tetrachloride, xylene, methylene chloride, and dichloroethane; forms sheets	31

*Here and henceworth the following abbreviations are employed: sol. = soluble; M = molecular weight; $T_{brittle}$, T_g, T_{soft}, T_{decomp}, and T_f are the embrittlement, glass, softening, and decomposition temperatures and the melting point respectively; cryst. = crystalline; amorph. = amorphous; DMFA = dimethylformamide; DMAA = dimethylacetamide; DMSO = dimethyl sulphoxide.

reactivity of the carboxyl carbon atom in these compounds to nucleophilic attack by water molecules is undoubtedly associated with the marked electron-acceptor influence of the perfluoromethylene chain.

The introduction of methylene groups between the carboxyl carbon atom and the perfluoroalkylene chain of the acidic component stabilises the polyesters with respect to hydrolysis [7].

Mixed polyesters obtained from perfluoroglutaric acid and hexafluoropentanediol, containing 2–5 mole % of non-fluorinated diacids or diols such ethylene glycol or 1,2-di(hydroxymethyl)carborane, were described in a recent patent [9]. These polymers are viscous liquids, and it has been suggested that after vulcanisation they can be employed as chemically stable elastomers.

Aliphatic polyesters of the third type have been investigated in greatest detail [6,10–14]. One of the examples of these polyesters, poly(hexafluoro-1,5-pentylene adipate)

$$[-OCH_2(CF_2)_3CH_2OCO(CH_2)_4CO-]_n,$$

has found industrial application in the manufacture of a special oil- and frost-resistant rubber. Although the thermal stability of the latter is not in fact very high, its capacity to retain elastic properties at fairly low temperatures is of some value. The working temperature range for this rubber is between −50° and 150°C. [15] Its degradation has been investigated [16–18].

In contrast to polyesters of the first and second types, some of the polyesters of the third type considered here, for example poly(hexafluoropentylene adipate), have fairly high molecular weights (about 20000)†. Such polyesters have been obtained by the reaction of fluorinated diols with aliphatic acid dichlorides; on the other hand, esterification with acids or their diethyl esters led only to low-molecular-weight polyesters.

All the aliphatic fluorine-containing polyesters synthesised are viscous liquids and rubber- or wax-like substances, many of which are insoluble in the usual organic solvents. It is suggested that the solubility of the polyesters falls with increasing total content of fluorine atoms in the molecule regardless of whether they are in the main or side chain [6].

A rubber-like vulcanised product based on the polyester from 4-oxa-2,2,3,3,5,5,6,6-octafluoroheptane-1,7-diol and adipic acid dichloride, which can be employed at low temperatures, has been described in an American patent [11]. Its embrittlement temperature is −58°C.

$$[-OCH_2(CF_2)_2O(CF_2)_2CH_2OCO(CH_2)_4CO-]_n.$$

In order to enhance the thermal stability while retaining an adequate flexibility of the macromolecule, polyesters containing aromatic units together with perfluoromethylene groups have been synthesised by the polycondensation of hexafluoropentanediol with derivatives of terephthalic [19], isophthalic [18,20], phthalic [18], and p-pentyloxyisophthalic [20] acids and also di-(p-carboxyphenyl) ether and 1,5-di-(p-carboxyphenoxy)pentane [18]. The polymers described in a British patent [19] have been suggested as thermostable casting resins and varnishes.

The possible mechanisms of the degradation of fluorine-containing polyesters have been discussed [18].

Mixed aromatic polyperfluoroalkylene esters, obtained by the joint polycondensation of hexafluoropentanediol with the dichlorides of isophthalic [12] and terephthalic acids [13], have also been described. It has been shown [12] that, following the introduction of 50 mole % of isophthaloyl units into the poly(hexafluoropentylene adipate) chain, the glass temperature of the polymer increases from −57° to −31°C and the rate of crystallisation falls appreciably. The introduction into the polymer chain of up to 30 mole % of terephthaloyl units hardly increases the glass temperature of the polymer (−62° and −60°C for the homopolymer and the copolymer), but the thermal stability increases slightly: the weight losses in a vacuum over a period of

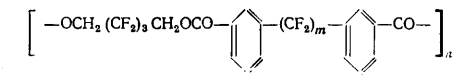
†The molecular weight was determined by measuring the viscosity of the melt by Flory's method and the characteristic constants of the equation relating the viscosity of the melts to the molecular weight of the polymer were found by titrating the terminal groups [6]. Subsequently the viscosities of the solutions of the polymers in chloroform were employed for this purpose [12]. The light-scattering method and measurements of the viscosity of dilute solutions of the polymer have also been employed [14] to determine the molecular weight.

2 h at 250°C are 32.6 and 26.65% for the homopolymer and the copolymer respectively[13].

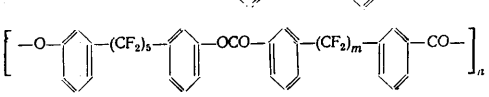
The polycarbonates obtained by the treatment with phosgene of a mixture of hexafluoropentanediol (80 to 95 mole %) and 2,2-di-(*p*-hydroxyphenyl)propane (20 to 5 mole %) have useful physical and chemical characteristics and are more readily worked into sheets and fibres than the corresponding non-fluorinated analogues[21].

In the 1960's hexafluoro-2,2-di-(*p*-hydroxyphenyl)-propane was employed as the fluorine-containing diol component for the synthesis of polyesters[22,29], polycarbonates[22,30], and polythiocarbonates[31]. Polyesters based on this diol and the dichlorides of isophthalic, terephthalic, and biphenyl-4,4′-dicarboxylic acids[22-29] and also polyesters based on trifluoromethyldi-(*p*-hydroxyphenyl)phenylmethane and the dichlorides of isophthalic and terephthalic acids[26,27] exhibit an enhanced stability with respect to thermal and thermo-oxidative degradation. Thus the temperatures of the onset of decomposition in nitrogen (data obtained by dynamic thermogravimetric analysis) of polyterephthalates obtained from the fluorine-containing diols hexafluoro-2,2-di-(*p*-hydroxyphenyl)-propane and trifluoromethyldi-(*p*-hydroxyphenyl)phenylmethane (438° and 446°C respectively) are higher than for the polyterephthalate obtained from 2,2-di-(*p*-hydroxyphenyl)propane (397°C).[27] On heating in air for 1 h at 400°C, these polymers lose 16.2, 11.5, and 26.3% of their weight respectively[32]. According to Ref. 29, sheet materials and aeroengine tubes made from polyesters and polycarbonates based on hexafluoro-2,2-di-(*p*-hydroxyphenyl)propane retain their characteristics after heating at 258°C for seven days.

Fluorine-containing polyesters based on the dichloride of 2,2-di-(*p*-carboxyphenyl)hexafluoropropane, which are distinguished by enhanced thermal stability, elasticity, and solubility, have also been described[27,28]. The synthesis of polyesters from *m*-derivatives of αω-diphenylperfluoroalkanes was reported in 1969.[33] Polyesters of the type



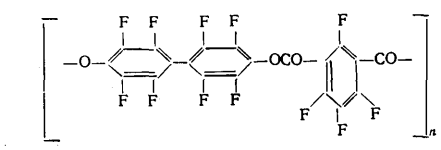
and



were obtained by the polycondensation of the dichlorides of -di-(*m*-carboxyphenyl)perfluoroalkanes with hexafluoropentanediol or αω-di-(*m*-hydroxyphenyl)perfluoropentane.

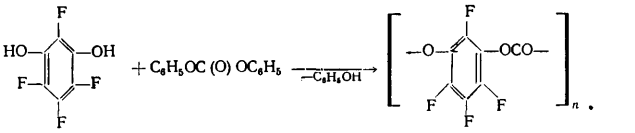
A polycarbonate based on αω-di-(*m*-hydroxyphenyl)-perfluoropentane has also been described[33]. The polymers synthesised in the same investigation have fairly low glass temperatures (16–45°C) and are elastomers above room temperature.

One of the attempts to modify the properties of polyesters consisted in their synthesis from aromatic perfluoro-compounds. A patent has been taken out[34] for high-molecular-weight polyesters which are resistant to thermal and thermo-oxidative degradation and which were synthesised by the interfacial polycondensation of octafluoro-4,4′-dihydroxybiphenyl with the dichlorides of tetrafluoroisophthalic and tetrafluoroterephthalic acids:



A similar polymer, consisting of a fluorinated analogue of Lavsan [a variety of nylon produced in the USSR (Ed. of Translation)] was obtained by the polycondensation of dimethyl tetrafluoroterephthalate and ethylene glycol; it differs little in its properties from Lavsan[35].

A patent[36] describes aromatic polyfluorocarbonates obtained by the polycondensation of tetrafluorophenylene bischloroformates with perfluorinated aromatic diols or 2,2-di-(*p*-hydroxyphenyl)propane. Poly(tetrafluoro-*m*-phenylene carbonate) was also synthesised by the polycondensation in the melt of tetrafluororesorcinol with diphenyl carbonate:



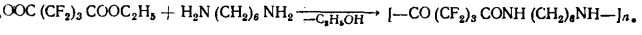
These polymers are suitable for the manufacture of articles designed for use at high temperatures.

III. FLUORINE-CONTAINING POLYAMIDE POLYMERS

1. Polyamides

The development of the chemistry of fluorine-containing polyamides was stimulated by the endeavour to synthesise a fluorinated analogue of nylon for the manufacture of fire-resistant fibres[37]. Like polyesters, fluorine-containing polyamides can be divided into three types. The polyamides and some of their properties are listed in Table 2.

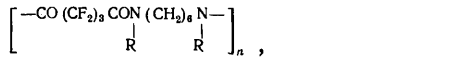
Aliphatic fluorine-containing polyamides were first described in patents at the beginning of the 1950's.[2,38] Polyamides of all three of the above types were obtained by the polycondensation of the diethyl esters or the dichlorides of alkane- and perfluoroalkane-dicarboxylic acids with hexamethylene- and 2,2,3,3,4,4,5,5-octafluorohexamethylene-1,6-diamine[38]. It proved possible to synthesise by this method only polyamides of the first type with a molecular weight (10 000) sufficient for the preparation from them of fibre-forming materials:



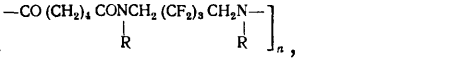
The fibres made from these polyamides have a high strength and density and are suitable for the manufacture of heavy fire-resistant fabrics. Analogous results were obtained in another study[39].

Later it was shown that, when solutions of diethyl perfluoroadipate are mixed with hexamethylenediamine, a low-molecular-weight polyamide is formed even in the cold, but its further polycondensation on heating in nitrogen or *in vacuo* is accompanied by degradation[40].

Fluorine-containing *N*-alkyl-substituted polyamides of the first type,



were synthesised by the polycondensation of secondary aliphatic diamines with dimethyl perfluoroglutarate, polyamides with the highest molecular weights being obtained from *NN′*-dimethyl and *NN′*-dimethyl-hexamethylenediamines. *N*-Substituted polyamides of the third type,



with a moderate molecular weight (degree of polymerisation 20–50%) could be obtained only from acid dichlorides, the reaction being carried out in a boiling inert solvent or in the presence of pyridine [41].

It was found that polyamides of the first type, like polyesters obtained from perfluoroalkanedicarboxylic acids, are hydrolysed very readily, the tendency towards hydrolysis decreasing somewhat with increasing dimensions of the substituent at the nitrogen atom [41].

It is noteworthy that chlorine-containing polyamides cannot be obtained by the polycondensation of hexamethylene- and octafluorohexamethylenediammonium salts of perfluoroadipic acid in the melt, since the salts decompose below the melting point. The attempts to achieve their polycondensation in the solid state at a temperature close to the melting point also failed to yield the expected results [39,40].

Although fluorine-containing diamines do not in fact form salts with weak acids owing to their low basicity, polyamides of the third type could nevertheless be obtained by heating the diamines with adipic acid [40,41].

In order to synthesise fluorine-containing polyamides of the first type, some investigators attempted to employ the methods of interfacial polycondensation using aliphatic [40,42,43] and aromatic [40] diamines and dichlorides of perfluoroalkanedicarboxylic acids. However, the polyamides obtained in this way proved to have low molecular weights. There is no doubt that the reason for the failure of these syntheses is the very ready hydrolysability of the dichlorides of perfluoroalkanedicarboxylic acids.

The high acylating capacity and volatility of such dichlorides made it possible to achieve the synthesis of fluorine-containing polyamides of the first type by a gas-phase polycondensation at the liquid–gas interface. High-molecular-weight fluorine-containing polyamides were obtained by passing the vapour of the dichloride of perfluoroadipic acid in a stream of nitrogen through aqueous solutions of aliphatic and aromatic diamines at 90–100°C. [40–46]

Attempts have been made to employ irreversible low-temperature polycondensation in amide solutions for the synthesis of fluorine-containing polyamides [47–49]. However, the aromatic polyperfluoroglutaramides obtained from the dichloride of perfluoroglutaric acid and benzidine or 3,3′-dihydroxybenzene in dimethylacetamide had very low molecular weights. Probably this is a consequence of the appreciably high rates of the competing reactions of dimethylacetamide with both the initial dichloride [50] and with the final acid chloride groups of the oligomers, resulting in chain termination.

A number of polyamides obtained from bifunctional derivatives of $\alpha\omega$-diphenylperfluoroalkanes have also been described. A thesis [51] mentions a high-melting polyamide made from hexamethylenediamine and 1,2-di-(*p*-carboxyphenyl)perfluoroethane. Mixed polyamides of this type with adipic or sebacic acid have been used to prepare thermostable fibres.

Recent patents [52,53] describe the synthesis of high-molecular-weight polyamides from *pp*′-dicarboxy- and *pp*′-diamino-derivatives of 2,2-diphenylhexafluoropropane. These polyamides are high-melting film-forming polymers with a comparatively high solubility.

Data on polyoxyamides and polyamides, obtained from derivatives of $\alpha\omega$-diphenylperfluoroalkanes and 2,2-diphenylperfluoropropane are presented in Table 2 and in Section IV, 2. A polyamide with aromatic perfluoro-units was obtained by heating octafluorobenzidine with pyromellitic dianhydride [54].

There has been only one study on the synthesis of fluorinated polyureas [55]. The polymers were obtained by the interfacial polycondensation of octafluorohexamethylenediamine with a number of di-isocyanates (hexamethylene, diphenylmethane, and toluylene di-isocyanates):

$$H_2NCH_2(CF_2)_4CH_2NH_2 + OCNRNCO \rightarrow [-NHCH_2(CF_2)_4CH_2NHCONHRNHCO-]_n .$$

The polymers synthesised had a low molecular weight and a relatively low thermal stability (decomposition temperature 215°C). [55]

2. Polyhydrazides

The possibility of obtaining low-molecular-weight fluorine-containing polyhydrazides from the dihydrazides and dichlorides of perfluoroalkane-dicarboxylic acids was first suggested by Brown in 1964 [61,62] (see Section IV, 2):

$$H_2NHNOC(CF_2)_mCONHNH_2 + ClOC(CF_2)_mCOCl \xrightarrow{-HCl} [-CONHNHCO(CF_2)_m-]_n .$$

High-molecular-weight aromatic poly(perfluoroalkylenebenzenedicarboxylic acid hydrazides) were synthesised by low-temperature polycondensation in amide solvents:



However, it was not possible to obtain high-molecular-weight fluorine-containing polyhydrazides by this method using the dichlorides of perfluoroalkanedicarboxylic acids. In order to avoid the chain termination of the macromolecules due to the considerable rate of reaction of the dichlorides of the strong perfluoroalkanedicarboxylic acids with the amide solvents, the dichlorides of aromatic acids were employed as the acid component and the dihydrazides of perfluoroalkanedicarboxylic acids as the diamine component (Table 3).

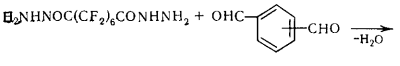
Aromatic poly(perfluoroalkylenebenzenedicarboxylic acid hydrazides) are amorphous polymers very readily soluble in the usual organic solvents; their softening temperatures are in the range 190–210°C and the temperatures of the onset of vigorous decomposition in air are between 250° and 300°C.

Polyisophthaloperfluoroglutarohydrazide, as well as polyisophthalohydrazide, form metal derivatives with zinc, nickel, and mercury salts.

Data on polyhydrazides based on 1,5-di-(*p*-carboxyphenyl)perfluoropentane [57] and 2,2-di-(*p*-carboxyphenyl)-perfluoropropane [63] are given in Table 3 and in Section IV, 2.

Fluorine-containing polyhydrazides are not of independent importance and are used as intermediates in the synthesis of certain polyazoles; the possibility of the cyclisation of fluorine-containing polyhydrazides into poly-1,3,4-oxadiazoles is discussed in Section IV, 2.

Fluorinated polymers obtained by the polycondensation of the dihydrazide of perfluorosuberic acid with isophthalaldehyde and terephthalaldehyde ($\eta_{inh} \simeq 0.1$) have also been described [64]:



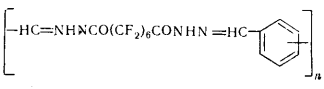


Table 2. Fluorine-containing polyamides.

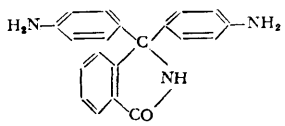
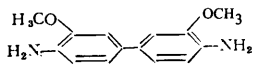
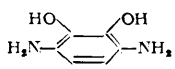
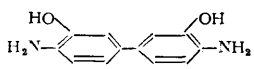
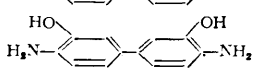
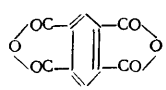
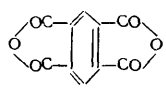
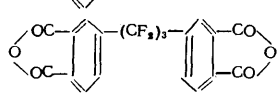
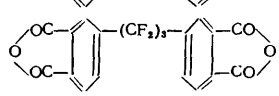
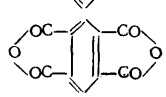
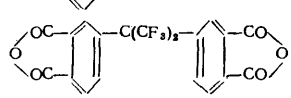
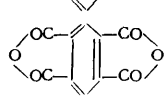
Initial component: amines	Initial component: acids and their derivatives	Certain properties of polymers	References
$(CH_2)_2(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.12$, $T_f = 280°C$	44—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_3(COOC_2H_5)_2$	$T_f = 183-185°C$	38
$(CH_2)_6(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.2-0.5$, $T_f = 210°C$	40, 42—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.08$, $T_f \simeq 200°C$; sol. in DMFA	38—40
$(CH_2)_6(NH_2)_2$	$(CF_2)_5(COCl)_2$		44—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_2CH_4COX)_2$*	$T_f = 400°C$	51
$(CH_2)_6(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl)_2$	$\eta_{inh} = 0.24$, $T_f = 280°C$; sol. in DMFA	53
$(CH_2)_8(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.21$, $T_f = 175-180°C$	40
$(CH_2)_{12}(NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$		42
$(CH_2)_6(NHCH_3)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 25-30°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_2H_5)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 5°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_3H_7\text{-}i)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 20°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_4H_9\text{-}n)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 20°C$; sol. in DMFA, benzene, iso-octane, and chloroform	41
$p\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.09$, $T_f = 378°C$ (decomp.)	40
$p\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.64$, $T_f > 380°C$	44—46
$m\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.46$	44—46
$p\text{-}C_6H_4(CH_2NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.10$, $T_f = 258-264°C$	40
$(C_6H_4NH_2\text{-}p)_2$	$(CF_2)_3(COCl)_2$	$\eta_{log} = 0.16$, $T_{decomp} = 250°C$	47—49
$m\text{-}C_6H_4(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.43$, $T_f = 370°C$ (decomp.); sol. in DMFA and DMAA	53
$1,2,6\text{-}C_6H_3(CH_3)(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.81$, $T_f > 350°C$	52
$(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.08$, $T_f > T_{decomp} \simeq 410°C$; sol. in DMFA and DMAA	53
$SO_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.7$, $T_f > 350°C$	52
$C(CH_3)_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.14$, $T_f > 400°C$	52
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.44$, $T_f > T_{decomp.} = 390°C$; sol. in DMFA and DMAA	53
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.1$, $T_f > 375°C$	52
$CF_2)_4(CH_2NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.11$, $T_f = 253°C$	40
$(CF_2)_4(CH_2NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.03$, $T_f = 231°-232°C$; sol. in DMFA	38, 40
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl_2)$	$\eta_{inh} = 0.7$, $T_f = 400°C$; sol. in DMFA and acetone	52, 53
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_4(COCl)_2$	$\eta_{inh} = 0.21$, $T_f = 216-223°C$	**40**
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.30$, $T_f = 219-221°C$; sol. in hot DMFA	**38, 40**
$(CF_2)_3(CH_2NHCH_3)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle} = 25-30°C$; sol in acetone and DMFA	41
$(CF_2)_3(CH_2NHC_2H_5)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle} = 20°C$; sol. in acetone, chloroform and DMFA	41

Table 2 cont'd

Initial component: amines	Initial component: acids and their derivatives	Certain properties of polymers	References
$(CF_2)_3(CH_2NHC_3H_7\text{-}iso)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle}$ = 30-35°C; sol. in acetone, chloroform, benzene, toluene, and DMFA	41
$(CF_2)_3(CH_2NHC_4H_9\text{-}n)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle}$ = 10-15°C; sol. in acetone, chloroform, benzene, toluene, ethyl acetate, and DMFA	41
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	η_{inh} = 0.6, T_f > 400°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	η_{inh} = 1.48, $T_f \simeq$ 370°C (decomp.); sol. in DMFA and DMAA	53
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	η_{inh} = 0.65, T_f = 348°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$1,3,5\text{-}C_6H_3(COCl)_2C_4H_9$	η_{inh} = 0.72, T_f > 350°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$1,3,5\text{-}C_6H_3(COCl)_2Cl$	η_{inh} = 0.74, T_f > 350°C	52
	$(CF_2)_3(COCl)_2$	η_{log} = 0.16	47, 48
	$(CF_2)_5(C_6H_4COCl)_2$	η_{log} = 0.8; sol. in amide solvents; d_{25}^4 = 1.54	56, 57
	$(CF_2)_6(C_6H_4COCl)_2$	η_{log} = 0.6; sol. in amide solvents, d_{25}^4 = 1.59	56, 57
$(CF_2)_6(C_6H_4NH_2\text{-}m)_2$		η_{log} = 1.5; sol. in amide solvents	56, 57
$(CF_2)_6(C_6H_4NH_2\text{-}m)_2$		η_{log} = 1.5; sol. in amide solvents	56, 57
$O(C_6H_4NH_2\text{-}p)_2$		η_{inh} = 1.65	33, 58, 59
$O(C_6H_4NH_2\text{-}m)_2$		η_{inh} = 0.51	33, 58
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$		η_{inh} = 0.6	60
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$		η_{inh} =0.52	60
$(C_6F_4NH_2\text{-}p)_2$			54

*In the original paper it is not stated whether the acid or its derivative was employed.

3. Polyurethanes

Fluorine-containing polyurethanes were first obtained in 1954 by heating hexafluoropentanediol with hexamethylene, toluylene, and octafluorotetramethylene di-isocyanates at 150°C.[65] These polyurethanes have been suggested as thermostable coatings. The fluorine-containing polyurethanes described in the literature and some of their properties are presented in Table 4.

Many polyurethanes containing fluorine in both the diol and in the di-isocyanate components of the molecule, including aromatic perfluoropolyurethanes have been described[66,67]. They were synthesised from fluorine-containing compounds in two ways: (1) by the reaction of di-isocyanates with diols (in solution and in the melt) and (2) by the reaction of diamines with bischloroformates (in solution under the conditions of interfacial polycondensation). For example, the synthesis of poly-[(*N*-hexafluorotrimethylene)hexafluoropentamethylene

Table 3. Fluorine-containing polyhydrazides.

Polymer unit	Certain properties	References
$-(CF_2)_3CONHNHCO-$		61, 62
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.26; sol. in alcohol, DMSO, and amide solvents; amorph.	48
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.84; sol. in alcohol, acetone, DMSO, and amide solvents	47, 48
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.86; sol. in methanol, DMSO, and amide solvents; amorph.	47, 48
$-NHNHCO-(CF_2)_4CONHNHCO-C_6H_4-CO-$	η_{log} = 0.89; sol. in alcohol acetone, DMSO, and amide solvents; amorph.	48
$-NHNHCO-C_6H_4-(CF_2)_3-C_6H_4-CONHNHCO-O-C_6H_4-CO-$	η_{log} = 0.35; sol. in DMSO and amide solvents	57
$-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-$	η_{inh} = 0.81; sol. in DMFA; T_{soft} = 340°C	63
$-NHNHCO-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-C_6H_4-CO-$	η_{inh} = 0.79; sol. in DMFA; T_{soft} = 360°C	63
$-NHNHCO-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-C_6H_4-CO-$	η_{inh} = 0.67; sol. in DMFA; T_{soft} = 330°C	63

dicarbamate] was achieved by heating hexafluorotrimethylene di-isocyanate with hexafluoropentanediol in ethyl acetate in the presence of triethylamine:

$$OCN(CF_2)_3NCO + HOCH_2(CF_2)_3CH_2OH \rightarrow [-NH(CF_2)_3NHC(O)OCH_2(CF_2)_3CH_2OCO-]_n \rightarrow$$
$$\xrightarrow{H_2O} HOOCCF_2COOH + H_2NCOOCH_2(CF_2)_3CH_2OCONH_2 .$$

This polyurethane is readily hydrolysed in air to hexafluoropentylene dicarbamate. On heating in the absence of moisture at 80–90°C, the polyurethane splits off hydrogen fluoride and is apparently converted into the polymer $[-N{=}CFCF_2CF{=}NCOOCH_2(CF_2)_3CH_2OCO-]_n$, which is somewhat more resistant to hydrolysis.

Polyurethanes in which a methylene group separates the perfluoroalkylene chain from the nitrogen atom, which some investigators believe makes them more resistant to hydrolysis, were synthesised by the reaction of fluorine-containing bischloroformates with diamines. Thus, on heating hexafluoropentamethylene bischloroformate with hexafluoropentamethylenediamine in ethyl acetate in the presence of pyridine, poly-[(*N*-hexafluoropentamethylene)-hexafluoropentamethylene dicarbamate] is formed:

$$ClOCOCH_2(CF_2)_3CH_2OCOCl + H_2NCH_2(CF_2)_3CH_2NH_2 \xrightarrow{-HCl}$$
$$\rightarrow [-NHCH_2(CF_2)_3CH_2NHCOOCH_2(CF_2)_3CH_2OCO-]_n .$$

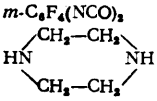
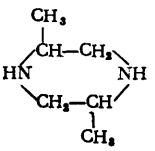
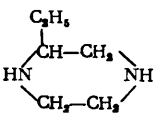
Under the conditions of interfacial polycondensation, the same reaction is accompanied by extensive hydrolysis of the bischloroformate. Unfortunately the authors do not quote experimental data for the hydrolytic stability for the polymer itself.

An aromatic perfluoropolyurethane was obtained by the reaction of tetrafluoro-*m*-phenylene di-isocyanate with tetrafluorohydroquinone in boiling xylene [66,67]. Among the fluorine-containing polyurethanes synthesised by Hollander and coworkers [66,67], the most thermostable is poly-[(*N*-tetrafluoro-*p*-phenylene)hexafluoropentamethylene dicarbamate], the decomposition temperature of which is about 300°C; other fluorine-containing polyurethanes decompose at about 200°C. [67]

The effect of fluorine atoms in the diol or di-isocyanate unit of the polymer on the properties of aliphatic polyurethanes was also investigated in other studies [68,69]. It was found, for example, that the polyurethane $[-NHCH_2(CF_2)_4CH_2NHCOO(CH_2)_6OCO-]_n$, containing in the di-isocyanate component a perfluoromethylene chain separated from the nitrogen atom by a methylene group, surpasses in its thermal stability the polyurethane $[-HN(CH_2)_6NHCOOCH_2(CF_2)_4CH_2OCO-]_n$ and a non-fluorinated analogue (weight losses *in vacuo* at 215°C over a period of 3.5 h about 1.5, 20, and 50% respectively). The first polyurethane is somewhat more resistant to the action of acids than the non-fluorinated polyurethane, but is inferior to it as regards resistance to the action of alkalis.

Polyurethanes based on fluorine-containing polyesters and polyethers with terminal hydroxy-groups [for example poly(hexafluoropentamethylene adipate), poly-hexafluoropentamethyleneformyl, etc.] and aromatic di-isocyanates or perfluorodi-isocyanates have also been

Table 4. Fluorine-containing polyurethanes.

Initial components		Certain properties of polymers	References
isocyanates and amines	glycols and bischloroformates		
$(CH_2)(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
$(CH_2)_8(NCO)_2$	$(CF_2)_4(CH_2OH)_2$	$[\eta] = 0.3$, $T_f = 126°C$; cryst.	69
1,3,5-$C_6H_4(CH_3)(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
p-$C_6H_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Solid; $T_f = 190-196°C$	66, 67
$(CF_2)_3(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Rubberlike substance	66, 67
$(CF_2)_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
$(CF_2)_3(CH_2NH_2)_2$	$(CF_2)_3(CH_2OCOCl)_2$	$T_{decomp} \simeq 200°C$ (air, helium)	66, 67
$(CF_2)_3(CH_2NH_2)_2$	p-$C_6F_4(OCOCl)_2$	$T_{soft} = 175-179°C$, $T_{decomp} \simeq 200°C$	66, 67
p-$C_6F_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Waxy substance; $T_f > 340°C$, $T_{decomp} \simeq 300°C$ (air, helium)	66
m-$C_6F_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Colourless solid; films formed from melt	66, 67
m-$C_6H_4(NCO)_2$	p-$C_6F_4(OH)_2$	Solid infusible substance; $T_{decomp} \simeq 200°C$ (air, helium)	66, 67
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_6(OCOCl)_2$	$[\eta] = 0.7$, $T_f = 184°C$; cryst.	68, 69
p-$C_6F_4(NCO)_2$	$(CH_2)_6(OCOCl)_2$	$T_f = 280-281°C$; cryst.	66, 67
m-$C_6F_4(NCO)_2$	$(CH_2)_6(OCOCl)_2$		66
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.57$, $T_f = 260°C$	75
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 1.60$, $T_f = 300°C$	75
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.82$, $T_f = 285°C$	75
m-$C_6H_4(NH_2)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.30$, $T_f = 238°C$	75
p-$C_6H_4(CH_2NH_2)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.40$	75
$CH_2(cis\text{-}C_6H_{10}NH_2\text{-}4)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 1.16$, $T_f = 210°C$	75
p-$C_6H_4[C(CH_3)_2NH_2]_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.33$, $T_f = 200°C$	75

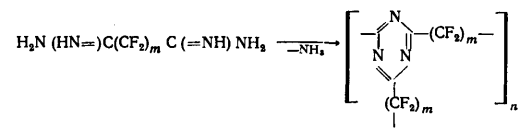
described. Polyurethanes obtained from polyperfluoroethers may find application as elastomers, coatings, adhesives, etc., i.e. whenever elasticity at low temperatures and high chemical stability are required [10,70,74].

A patent was published in 1968 describing the synthesis of high-molecular-weight polyurethanes based on the bischloroformate of 2,2-di-(4-hydroxyphenyl)hexafluoropropane and various diamines. It is suggested for the manufacture of light-resistant flexible sheets and crease-resistant fibres [75].

IV. FLUORINE-CONTAINING POLYAZOLES

1. Poly-1,3,5-triazines

The first examples of the class of polyperfluoroalkylene-heterocycles, namely polyperfluoroalkylene-1,3,5-triazines, were obtained towards the end of the 1950's and at the beginning of the 1960's by the homocondensation of the diamidines or imidines of perfluoroalkanecarboxylic acids and their copolycondensation with the monoamidines of perfluoroalkanecarboxylic acids [76-80]. Thus, on heating perfluoroadipodiamidine or perfluoroglutarimidine above the melting point, solid insoluble and infusible cross-linked polymers are formed:

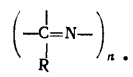


The use of mixtures of a diamidine (or imidine) with a monoamidine for polycondensation leads to the formation of partly cross-linked polymers, the degree of cross-linking and the properties of which depend on the molar ratios of the components and the length of their perfluoromethylene chain. The copolymers are either elastomeric materials with a low strength or they are rigid non-elastic

polymeric substances. All polyperfluorotriazines have a very high chemical stability and a high resistance to thermal and thermo-oxidative degradation. For example, the copolymers of perfluoroadipodiamidine or perfluoroglutarimidine with perfluorobutyramidine (1 : 1) are stable on heating in air at 350°C for about 72 h. Boiling in fuming nitric acid for 24 h leads only to a change of their colour from yellow to white.

The thermal degradation of polyperfluoroalkylenetriazines was investigated by a number of workers. It has been shown [81,82] that the activation energy for the degradation reactions of these polymers (homo- and co-polymers) is about 30–40 kcal mole^{-1} below 500°C, which is much less than the activation energy for the thermal decomposition of Teflon (about 80 kcal mole^{-1}); at about 500°C the rates of their decomposition are lower than that of Teflon.

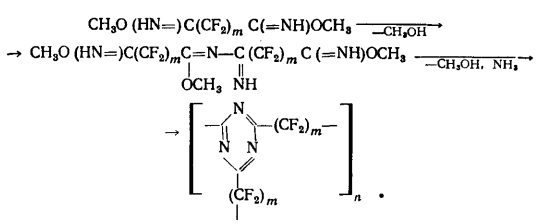
Other investigations [83] showed that the rate of degradation of polyperfluoroalkylenetriazines at 350–500°C *in vacuo* falls rapidly with increasing conversion up to 30% and then remains almost constant up to complete volatilisation of the polymer. While the rate of degradation in the initial stage is comparable with the rate of degradation of Teflon, in the second stage it is much lower. The authors suggest that the high rates of degradation in the initial stages are due to the amide groups, which are always present in the polymers. The decomposition of their amide groups results in the formation of water, which hydrolyses the triazine rings, and radicals, which cause their polymerisation with formation of a polyene structure:



After the amide groups have been consumed, the main degradative pathway reduces to the depolymerisation of the comparatively short perfluoroalkylene fragments of the macromolecule with chain transfer by the transalkylation of the triazine rings. The rates of these reactions are lower than the rate of depolymerisation of Teflon.

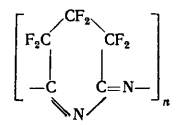
Since polyperfluoroalkylenetriazines were of greater interest as very promising elastomers [84], the efforts of many investigators were directed to the development of other methods for their synthesis, including methods for the synthesis of polytriazines with a linear structure.

Cross-linked polyperfluoroalkylenetriazines similar to those described above were obtained by the thermal homopolycondensation of dimethyl perfluoroglutarimidate and dimethyl perfluoroadipimidate and their "dimers": [85–87]



Later a similar conversion of dimethyl perfluoroglutarimidate into a cross-linked triazine polymer was also described in another study [88].

The trimerisation reaction of the dinitriles of perfluoroalkanedicarboxylic acids, the possibility of which in the presence of acid or alkaline catalysts and had been pointed out previously [79], was investigated. The homopolycyclisation of perfluoroglutarodinitrile under a high pressure (about 20 000 kgf cm^{-2}) in the presence of ammonia or secondary amines at 276°C leads to polytriazines. When the pressure is reduced, the formation of polymers with the structure [89]



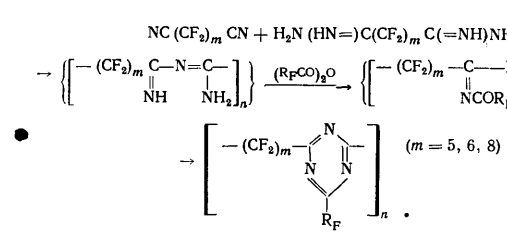
predominates.

A method for the preparation of cross-linked polytriazines by the polycyclisation of fluorine-containing dinitriles in the presence of metals (copper, iron, etc.) at 190°C has been described [90]. Polycondensation of perfluoroglutarodinitrile in the presence of metal oxides (Ag_2O, HgO, etc.) leads to a low-molecular-weight polymer (ηinh = 0.03) containing the group $-C=N-C=N-$. [91,92]

A method for the preparation of polytriazine by the thermal homopolycondensation or copolycondensation of perfluorodinitriles containing ether linkages [for example, 2,7-dicyano-3-oxaperfluoroheptane $NCCF(CF_3)O(CF_2)_4CN$ and 2,10-dicyano-3,9-dioxaperfluoroundecane $NCCF(CF_3)O(CF_2)_5OCF(CF_3)CN$] in the presence of ammonia has been patented. The cotrimerisation of the above dinitriles with diamidines derived from them or of diamidines with mononitriles (for example, with perfluoroacetonitrile and perfluoro-2-propoxypropionitrile) in an amount of 0.5–30% has also been described. In contrast to the polymers obtained from derivatives of perfluoroalkanedicarboxylic acids, these resins have satisfactory mechanical characteristics, which allows their use for the manufacture of mechanically strong articles [93,94].

A patent [95] proposes a method for the synthesis of perfluoroalkylenetriazines by heating at 50°C a mixture of perfluoroglutarothioamide with perfluorobutyronitrile in the presence of triethylamine.

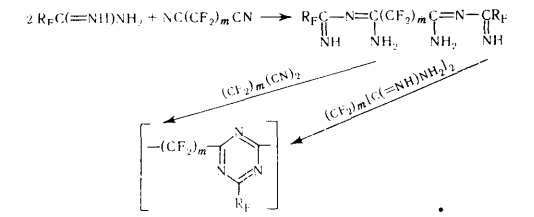
The first reports of the synthesis of linear polyperfluoroalkylenetriazines were published almost simultaneously by a number of investigators. According to the method proposed by Dorfman et al. [96] and by Griffin [97], the reaction of diamidines of perfluoroalkanedicarboxylic acids with dinitriles of perfluoroalkanedicarboxylic acids was used to synthesise initially at room temperature linear imidoylamidine polymers which, without isolation, were acylated and cyclodehydrated by anhydrides of perfluorocarboxylic acids to polyperfluoroalkylenetriazines:



This method was employed to synthesise from derivatives of perfluoroalkanedicarboxylic acids linear-high-molecular-weight polytriazines (degree of polymerisation about 300), which are soluble yellow rubberlike polymers with a glass temperature between −5 and −17°C and a decomposition temperature of about 420°C (differential thermal analysis).

The attempt [96] to obtain an imidoylamidine polymer by the reaction of dinitriles with ammonia without isolating the diamidines yielded only low-molecular-weight products.

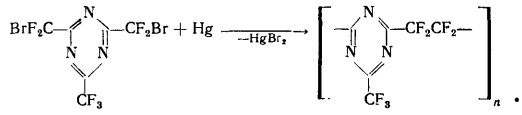
In another method [97,98] a stable intermediate bisimidoylamidine compound is initially obtained from a monoamidine and a dinitrile and isolated in the solid state; after purification it is refluxed in benzene with a diamidine or a dinitrile until the formation of a linear elastomer:



If the above processes are carried out without the isolation and purification of the intermediate, a gel is formed.

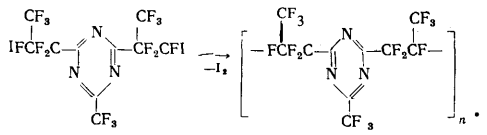
Methods have also been proposed for the preparation of polyperfluoroalkylenetriazines from monomers already containing triazine rings.

An interesting method has been described [91,97,99,100] for the preparation of a high-molecular-weight polytriazine from 2,4-di(bromodifluoromethyl)-6-trifluoromethyltriazine by heating it with mercury in evacuated tubes at 200°C (degree of polymerisation about 350):



An analogous polymer was obtained [100] by the same method from 2,4-di(difluoroiodomethyl)-6-difluoromethyltriazine. According to Griffin [97], the polymer exhibits elastic properties above 40°C. The author suggests that the glass temperature of this polymer may be reduced by introducing into the triazine rings of the macromolecules longer perfluoroalkyl substituents.

A polytriazine elastomer has been obtained by the radical polycondensation of di(iodoperfluoroalkyl)triazine under the influence of ultraviolet light:



The scope of this method is limited by the low availability of the initial di-iodide.

The thermal and chemical stabilities of linear high-molecular-weight polytriazines are comparable to the stability of cross-linked polymers but, as was expected, their mechanical strength proved to be much higher (the tensyl strength of linear polytriazine is 98 kgf cm^{-2} [97] against 7–35 kgf cm^{-2} [96] for cross-linked polymers).

The possibility of obtaining polytriazines from monomers containing triazine rings and cyanoperfluoroalkyl groups is considered in a brief report [90].

2. Other Polyazoles

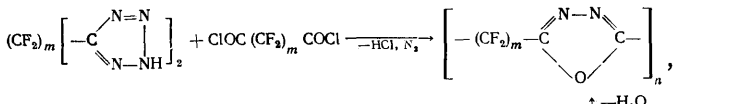
Simultaneously with the development of methods for the synthesis of linear polyperfluoroalkylene-1,2,3-triazines, the possibility of synthesising other high-molecular-weight linear polyperfluoroalkyleneazoles was investigated.

Numerous model perfluoroalkyl-substituted heterocyclic systems were obtained even earlier and it was established that their chemical and thermal stabilities are comparable to those of fluorinated triazine systems [80,101].

Towards the first half of the 1960's, methods of synthesising various high-molecular-weight linear polyazoles containing aliphatic and aromatic units in the macromolecular chain were already known. It was possible to postulate that the use of these methods for the synthesis of fluorine-containing polyazoles will make the latter more readily available than linear polytriazines.

Indeed, soon after the first publications on cross-linked polyfluoroalkylenetriazines, several communications appeared on the synthesis of other fluorine-containing polyazoles: poly-1,3,4-oxadiazoles, polybenzoxazoles, polybenzimidazoles, etc. These polyazoles were linear polymers with relatively low molecular weights.

The synthesis of polyperfluoroalkylene-1,3,4-oxadiazoles was achieved by two methods [61,62,102]; in the first method polyoxadiazoles were obtained by treating solutions of bistetrazoles in pyridine or acetonitrile with dichlorides of perfluoroalkanedicarboxylic acids:

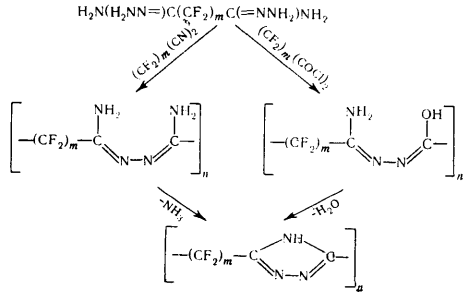


A polyoxadiazole (η_{inh} = 0.1), which behaves as an elastomer in the range 65–120°C and is inert at 100°C to the action of concentrated sulphuric and nitric acids, was synthesised in this way from perfluorohexane-1,6-bistetrazole and the dichloride of perfluorosuberic acid [61,62,102].

In the second method, polyhydrazides, which were subsequently converted into polyperfluoroalkyleneoxadiazoles, were obtained from the dihydrazides and dichlorides of perfluoroalkanedicarboxylic acids. The conditions for the preparation of the polyhydrazides and their cyclisation and also the characteristics of the polymers were not quoted [61,62] apart from the mention of a comparatively low molecular weight.

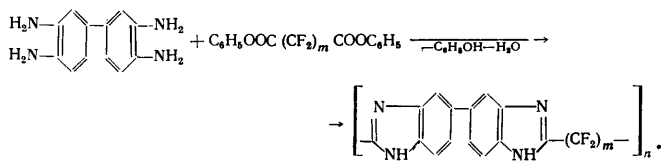
It is noteworthy that aromatic polyperfluoroalkylenehydrazides (see Section III, 2) do not undergo thermal cyclisation to polyoxadiazoles. Chemical cyclodehydration of these polyhydrazides with phosphorus oxychloride is accompanied by marked degradation and leads to low-molecular-weight compounds [48].

Two pathways for the preparation of polyperfluoroalkylene-1,2,4,4*H*-triazoles from perfluoroalkylenediacyldihydrazidines have been indicated [62]:



In the first method perfluoroalkylenediacyldihydrazidine reacts with a perfluoroalkylenedinitrile giving a polymer, which is converted into poly-1,2,4,4*H*-triazole with liberation of ammonia. In the second method perfluoroalkylenediacyldihydrazidine is acylated by the dichloride

of a perfluoroalkanedicarboxylic acid and the resulting polymer is dehydrated to poly-1,2,4,4*H*-triazole. These methods of synthesis of triazoles are similar to the modern methods for the synthesis of linear polyperfluoroalkylenetriazines from the diamidines of perfluoroalkanedicarboxylic acids (see Section IV, 1). In 1964 a number of investigators described almost simultaneously the synthesis of low-molecular-weight polyperfluoroalkylenebenzimidazoles by the polycondensation in the melt of 3,3-diaminobenzidine with the diphenyl esters of various perfluoroalkanedicarboxylic acids [103-105]:

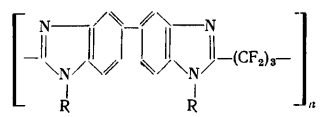


Contrary to expectation, these polymers proved to be inadequately thermostable and their degradation with liberation of hydrogen fluoride was observed in the polycondensation process itself in an atmosphere of argon below 250°C. [104,105] According to thermogravimetric data, the temperature of the onset of vigorous decomposition of polyperfluoroalkylbenzimidazoles in nitrogen does not exceed 300°C. [103] It has been noted [104] that polycondensation with perfluoroglutaric acid (at 220–250°C) leads to marked charring of the reaction mixture.

In the polycondensation of 3,3′-diaminobenzidine with both perfluoroglutaric acid and with its diphenyl ester, the evolution of not only hydrogen fluoride but also carbon dioxide was observed [106].

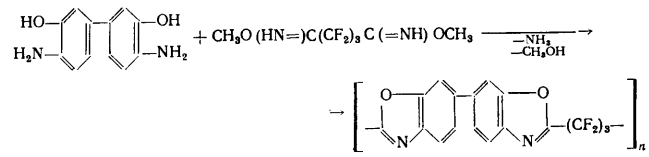
The comparatively low thermal stability of poly-2,2′-(perfluoroalkylene)-5,5′-dibenzimidazoles can be explained by a dehydrofluorination reaction, which is attributed mainly to the mobility of the hydrogen atoms in the imino-groups of the benzimidazole rings [104,107]. This hypothesis was confirmed to some extent by the appreciable increase of the decomposition temperatures of model *N*-methyl- and *N*-phenyl-substituted 2-perfluoroalkylbenzimidazoles ($T_{decomp} \simeq 390$–450°C) compared with unsubstituted 2-perfluoroalkylbenzimidazoles ($T_{decomp} \simeq 300$°C). [49,107]

N-Substituted fluorine-containing polybenzimidazoles were obtained by the polycondensation in the melt of 4,4′-di(methylamino)-3,3′-diaminobiphenyl and 4,4′-dianilino-3,3′-diaminobiphenyl with diphenyl perfluoroglutarate [49]:



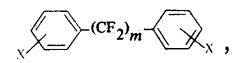
The study of their thermal stability *in vacuo* and in air showed that only phenylation at nitrogen leads to some improvement of thermal stability: poly-(*NN*′-diphenyl-2,2′-perfluorotrimethylene-5,5′-dibenzimidazole) begins to decompose very slowly at about 350°C in air and *in vacuo*. The appreciable difference between the behaviour of model fluorine-containing benzimidazoles and the corresponding polymers can be explained by the presence in the latter of a relatively large number of terminal amino-groups as a result of their low molecular weight.

It was found useful to attempt the replacement of the imino-group in the ring by an oxygen atom, i.e. to obtain a benzoxazole structure. A low-molecular-weight poly-2,2′-perfluorotrimethylene-6,6′-dibenzoxazole was obtained by the polycondensation of 3,3′-dihydroxybenzidine with dimethyl bisiminoperfluoroglutarate in *N*-methylpyrrolidone at 190°C; its properties were not investigated [108]:



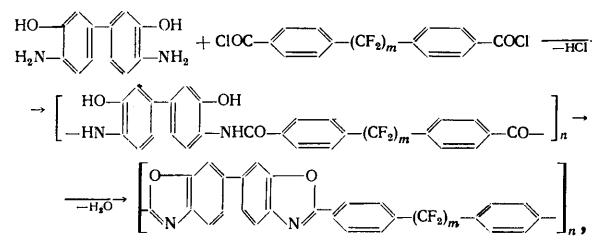
It follows from the above that fairly numerous attempts to achieve the synthesis of polyazoles with perfluoromethylene bridges in the chain from derivatives of perfluoroalkanedicarboxylic acids led only to low-molecular-weight polymers (with the exception of polytriazines).

High-molecular-weight linear polyperfluoroalkyleneazoles were obtained successfully for the first time from derivatives of $\alpha\omega$-diphenylperfluoroalkanes—monomers with functional groups of the type



where X = *p*-COCl, *m*-NH_2, etc., "screened" from the perfluoromethylene chain. In these compounds thermostable benzene rings serve as a "screen" [33,56-59,109].

Thus high-molecular-weight polybenzoxazoles were obtained by a two-stage synthesis from the dichlorides of $\alpha\omega$-di-(*p*-carboxyphenyl)perfluoroalkanes and 3,3′-dihydroxybenzidine via poly-*o*-hydroxyamides with their subsequent thermal cyclisation (250–300°C) in a vacuum or by chemical treatment (polyphosphoric acid, 200°C). [56,57,109] The polybenzoxazoles synthesised by the first method,



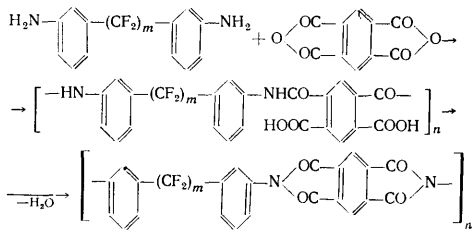
are insoluble, probably owing to partial cross-linking. On cyclisation under milder conditions in polyphosphoric acid, soluble polymers are formed ($\eta\log = 0.5$–1.3). However, under these conditions there is partial hydrolysis of CF_2 groups adjacent to the benzene rings.

High-molecular-weight soluble polybenzimidazoles ($\eta\log = 1.1$–1.6) were synthesised by the polycondensation in the melt of 3,3′-diaminobenzidine with diphenyl esters of $\alpha\omega$-di-(*p*-carboxyphenyl)perfluoroalkanes [56,57,109].

Polyperfluoroalkylene-1,3,4-oxadiazole was obtained by the condensation of the dihydrazide of 1,5-di-(*p*-carboxyphenyl)perfluoropentane with isophthaloyl chloride in hexamethylphosphoramide followed by cyclisation of the resulting polyhydrazide [57,109]. In contrast to the polyhydrazides obtained from derivatives of perfluoroalkanedicarboxylic acids [48], heat treatment of this polyhydrazide resulted in its conversion into a poly-1,3,4-oxadiazole.

High-molecular-weight polyperfluoroalkyleneimides have been synthesised by various investigators from

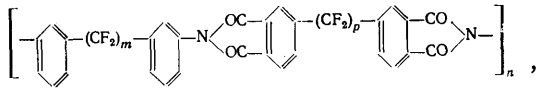
derivatives of αω-diphenylperfluoroalkanes in two ways—by a two-stage synthesis [33,57-59,109] and by polycondensation in the melt [33,58]:



Thus reaction of αω-di-(*m*-aminophenyl)perfluoroalkanes with pyromellitic dianhydride [57,109] and also of di-(*m*-aminophenyl) [33,58] and di-(*p*-aminophenyl) ethers [33,58,59] with the dianhydride of 1,3-di-(3′,4′-dicarboxyphenyl)perfluoropropane in dimethylacetamide yielded polyamides which were then cyclised to the corresponding polyimides either by heat treatment or by treatment with a mixture of acetic anhydride and pyridine [33,57,58,109]. The polyimides based on pyromellitic dianhydride are soluble only in concentrated nitric acid ($d = 1.5$), probably with decomposition ($\eta\log \simeq 0.3$); the polymers based on di(aminophenyl) ethers are sparingly soluble in dimethylacetamide ($\eta_{inh} = 0.56$ and 1.31 for *m*- and *p*-derivatives respectively), their softening temperatures lying in the range 190–240°C.

The variation of the glass temperature with the composition of the copolymers of di-(*p*-aminophenyl) ether with pyromellitic dianhydride and the dianhydride of 1,3-di-(3′,4′-dicarboxyphenyl)perfluoropropane has been investigated [59].

Polyimides containing fluorine atoms in both components ($\eta_{inh} = 0.5–1.7$, $M > 30\,000$),



where $m = 3$ or 5 and $p = 3$, 4, or 7, have been synthesised by the polycondensation in the melt of αω-di-(*m*-aminophenyl)perfluoroalkanes with the dianhydrides of αω-di-(3′,4′-dicarboxyphenyl)perfluoroalkanes [33,58]. The ready solubility of these polyimides in amide solvents and in chlorinated hydrocarbons and also the comparatively low softening temperatures (135–180°C), above which they behave as elastomers, are noteworthy.

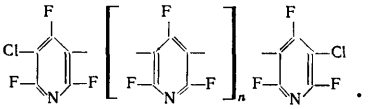
Polybenzoxazoles and polyimides form strong sheets [57,58].

Polyazoles based on derivatives of αω-diphenylperfluoroalkanes begin to decompose in air at about 350 to 400°C [57] (data derived from dynamic thermogravimetric analysis) and are thus somewhat inferior in their thermal stability in air to aromatic polyazoles.

All the above data show that the synthesis of aromatic polyperfluoroalkyleneazoles from derivatives of αω-diphenylperfluoroalkanes with different functional groups is the most general method for the preparation of linear high-molecular-weight polyperfluoroalkyleneazoles containing perfluoromethylene units in the main chain.

There exists also patent data concerning the synthesis of polyimides [60] and poly-1,3,4-oxadiazoles [63] with hexafluoropropyldiene bridges by a two-stage method. Polyazoles fluorinated in both components are distinguished by an unusually high solubility while retaining a high thermal stability: $T_{decomp} \simeq 460–475$°C; T_g (polyimide) ≃ ≃ 340°C.

Brief reports have been published recently on the use of aromatic polyfluoro-derivatives for the synthesis of fluorine-containing polyazoles. Thus poly-1,3,4-oxadiazole has been obtained from the dichloride of tetrafluoroterephthalic acid [35]. A patent [110] (see also Dine-Hart and Wright [54]) describes a synthesis of polypyromellitimides from *m*- and *p*-tetrafluorophenylenediamines, octafluorobenzidine, and pyromellitic dianhydride. Articles made from these polymers can be used for a long time at high temperatures. Polyperfluoropyridine ($n = 15–16$) has been obtained as a solid with m.p. 180–190°C by heating 3,5-dichlorotrifluoropyridine in dimethylformamide in the presence of activated copper [111]:

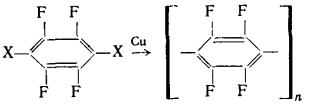


The above data on fluorinated polyazoles evidently show that studies not only on triazine polymers but also on other polyazoles are being vigorously pursued.

V. FLUORINE-CONTAINING POLYPHENYLENE POLYMERS

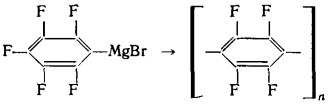
1. Polyphenylenes

A low-molecular-weight polyperfluoro-*p*-phenylene ($M \simeq 1700$, $T_{soft} > 360$°C) was first obtained in 1955 [112] by the Ullmann reaction in which 1,4-dibromo- or 1,4-di-iodo-tetrafluorobenzene was heated with activated copper powder. The use of 1,4-dichlorotetrafluorobenzene in this reaction leads to the same results [113]:



where X = Cl, Br, or I.

A polyperfluoro-*p*-phenylene with a relatively high molecular weight was synthesised by the decomposition of pentafluorophenylmagnesium bromide in boiling tetrahydrofuran (THF), the properties of the polymers formed depending on the temperature at which the initial organomagnesium compound had been obtained [114,115]. Thus if the latter was obtained at −30°C, a soluble polymer with $M \simeq 15\,000$ is formed, while the organomagnesium compound obtained at a higher temperature yields mainly an insoluble polymer. An insoluble polyperfluorophenylene infusible up to 360°C has also been obtained by the decomposition of pentafluorophenylmagnesium chloride [114,116]:



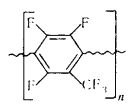
The predominantly *p*-phenylene structure of the polymer was confirmed by the isolation of perfluoroquaterphenyl from the reaction products [114]. A method for the preparation of polyperfluorophenylenes, probably with a *p*-phenylene structure, by decomposing perfluorophenylmagnesium

chloride in boiling tetrahydrofuran in the presence of decafluorobiphenyl, has been suggested in a patent [117]. In the presence of a tenfold excess of the organomagnesium compound, a polyphenylene with a degree of polymerisation of about 25 is obtained.

It is noteworthy that attempts to achieve the synthesis of a polyphenylene by the polycondensation of 1,4-dibromo- and 1,4-di-iodo-tetrafluorobenzene in the presence of sodium or zinc [112] and also by the decomposition of organolithium and organomagnesium compounds derived from 1,4-dibromo- and 4-bromo-tetrafluorobenzene [114] did not lead even to low-molecular-weight polymers of this type.

Polyperfluoro-*m*-phenylene was synthesised simultaneously by a number of workers [114,117-119] by heating 1,3-dibromo- or 1,3-dichlorotetrafluorobenzene with activated copper in decafluorobiphenyl or dimethylformamide and also in the absence of solvents; the reaction with the 1,3-dibromo-derivative leads to the formation of a polymer with a much higher molecular weight (up to about 16 000, $T_{soft} \simeq 300°C$) and requires lower temperatures. Polyperfluoro-*m*-phenylene is more soluble and melts at a lower temperature than polyperfluoro-*p*-phenylene. It is interesting that their thermal stabilities are approximately the same. According to Thrower and White [118], polyperfluoro-*m*-phenylene may prove to be more readily available than its non-fluorinated analogue because of the high reactivity of 1,3-dibromotetrafluorobenzene.

Low-molecular-weight polyperfluorophenylenes ($M \simeq 1500$, $T_{soft} \simeq 200°C$) containing simultaneously 1,3- and 1,4-phenylene units have also been described. They are obtained by the reaction of 1,3-tetrafluorophenylene-dimagnesium dibromide with decafluorobiphenyl (in molar proportions of 2 : 1) in boiling tetrahydrofuran [114]. High-molecular-weight polyperfluorotolylenes,



(M up to 200 000), have been synthesised by the decomposition of 2-heptafluorotolylmagnesium chloride in boiling tetrahydrofuran. They do not melt up to 300°C and their solubility in organic solvents is much higher than that of polyperfluorophenylenes [62,114,120].

High-molecular-weight polyperfluorophenylenes, like polyperfluorotolylenes, are stable in a vacuum up to about 600°C: under the conditions of oxidative degradation, they are less stable and begin to decompose vigorously at about 400°C. The thermal stability of polyperfluorophenylenes *in vacuo* is comparable with that of non-fluorinated polyphenylenes and poly(phenylene oxides), but is lower than the thermal stability of polytetrafluoroethylene.

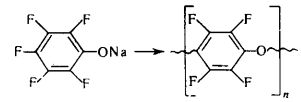
The resistance of polyperfluorophenylenes to thermo-oxidative degradation is inferior to that of the above polymers [62,114,115,121].

It has been noted that, when polyperfluorophenylenes are heated initially in a vacuum at 400°C, their resistance to oxidative degradation is greatly improved.

2. Polyphenylenes with Bridging Groups

Since polyperfluorophenylenes are fairly rigid systems, attempts have been made to improve their flexibility by introducing various atoms or groups of atoms, such as O, S, OCF_2, and others, between the phenyl rings.

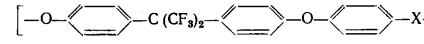
a. Polyoxy(phenylenes). Polyoxy(perfluorophenylenes) were first obtained in 1958 by the thermal decomposition of alkali metal pentafluorophenoxides [122,123]:



According to Pummer and Wall [123], the polymers are formed as a result of nucleophilic attack on the carbon atom adjacent to the fluorine atom by the growing phenoxide anion and they probably contain both 1,3- and 1,4-phenylene units.

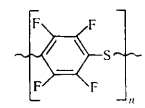
The decomposition of pentafluorophenoxides is carried out in three ways: in the absence of solvents, in an aqueous medium, and in pentafluorophenol [123]. In the first two cases low-molecular-weight polymers are formed. A high-molecular-weight polymer ($M \simeq 12\,500$) has been obtained by heating an excess of sodium pentafluorophenoxide with pentafluorophenol. Polyoxy(perfluorophenylene) is a low-melting vitreous material ($T_{soft} > > 100°C$) soluble in the usual organic solvents: on heating *in vacuo* (260°C, 18 h), it becomes insoluble and acquires rubberlike properties in the temperature range 90 to 300°C. [114] Polyoxy(perfluorophenylene) is much less stable than its non-fluorinated analogue and polyperfluorophenylenes: on heating *in vacuo* for 30 min at 400°C it loses about 47–50% of its weight [114].

Aromatic polyesters with perfluoroisopropylidene units,



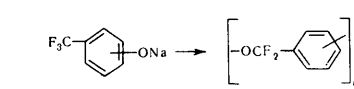
where (I) X = SO_2, $T_g = 205°C$, and $T_f = 255°C$ and (II) X = CO and $T_g = 175°C$, have been obtained by the polycondensation of alkali metal phenoxide derivatives of 2,2-di-(*p*-hydroxyphenyl)perfluoropropane with di-(4-fluorophenyl) sulphone or 4,4'-difluorobenzophenone in aprotic solvents at 130–140°C. [124]

b. Polythioperfluorophenylenes. Low-molecular-weight polythioperfluorophenylenes,



have been synthesised in two ways [125]: by the reaction of hexafluorobenzene with sodium sulphide (the polymer has the 1,4-structure with a degree of polymerisation of about 10) and by the thermal decomposition of sodium pentafluorophenoxide. In contrast to polyoxyperfluorophenylene, polythioperfluorophenylene is insoluble in the usual organic solvents and does not melt up to about 300°C. [114] The thermal stability of polythioperfluorophenylene is lower than that of polythiophenylene. It begins to decompose vigorously below 400°C under the conditions of both thermal and thermo-oxidative degradation: the formation of a large residue indicates a significant role of chain-transfer reactions [126].

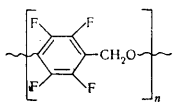
c. Polyoxybenzylenes and polythiobenzylenes. Poly-*o*- and poly-*p*-oxy-$\alpha\alpha$-difluorobenzylenes were first obtained by heating *o*- and *p*-trifluoromethylphenols with cold dilute alkali [127]:



According to the authors, this reaction proceeds via pseudoquinonoid structures, since *m*-trifluoromethylphenol, which is incapable of forming structures of this kind, is resistant to the action of aqueous alkali.

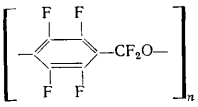
Poly-*p*-oxy-$\alpha\alpha$-difluorobenzylene has also been synthesised by the thermal dehydrofluorination of *p*-trifluoromethylphenol *in vacuo* at 900–950°C, the polymer being formed on the surface of a cold trap in the form of a weakly coloured film [128]. Poly-*p*-oxy-$\alpha\alpha$-difluorobenzylene is sparingly soluble in the usual organic solvents and is resistant to the action of concentrated alkalis.

Poly-oxy-2,3,5,6-tetrafluorobenzylene,



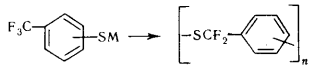
synthesised by refluxing 2,3,4,5,6-pentafluorobenzyl alcohol of 2,3,4,5,6-pentafluorobenzyl bromide with aqueous potassium hydroxide, has been described [129,130]; its melting point is 180–190°C. [130]

A third example of fluorine-containing polyoxybenzylenes is poly-*p*-oxy-perfluorobenzylene:



which was synthesised by a number of investigators by heating heptafluoro-*p*-cresol with aqueous bases at 100°C. [114,131,132] Later polyoxyperfluorobenzylene was obtained by the thermal dehydrofluorination of heptafluoro-*p*-cresol *in vacuo*. [128] The mechanism of the formation of the polymer was not elucidated by the authors. The maximum molecular weight of polyoxyperfluorobenzylene is about 3000–5000; it is soluble in the usual organic solvents and its softening temperature varies in the range 65–120°C depending on the molecular weight. Like polyoxyperfluorophenylene, polyoxyperfluorobenzylene gives rise on heating *in vacuo* at about 200°C to a polymer with elastic properties at temperatures above 100°C. The thermal stability of polyoxyperfluorobenzylene is approximately the same as that of polyoxyperfluorophenylene: the weight loss at 350°C in 1 h is 89%.

A method for the preparation of poly-*m*- and poly-*p*-thio-$\alpha\alpha$-difluorobenzylenes has been patented:



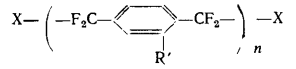
It involves heating Group I metal *m*- or *p*-($\alpha\alpha\alpha$-trifluoromethyl)thiophenoxides at 200°C for 5 days; the reaction may be carried out in pyridine solution. Poly-*m*-thiodifluorobenzylene (degree of polymerisation 12) melts at 285–310°C. [133]

d. Poly-*p*-xylylenes. Poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene,

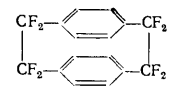


was first synthesised by the pyrolysis of $\alpha\alpha$-dibromo-$\alpha\alpha\alpha'\alpha'$-tetrafluoro-*p*-xylylene in a vacuum at 330°C in the presence of zinc in the form of an amorphous film on the surface of a trap cooled to −78°C; the conversion of the initial monomer into the polymer is about 8% and the softening temperature of the polymer is 380°C. The authors suggest that $\alpha\alpha\alpha\alpha$-tetrafluoro-*p*-quinodimethane, which is stable in the gas phase but polymerises rapidly in the liquid phase, is an intermediate in the reaction [134]. Other investigators believe [135] that the reaction can also proceed via the free biradicals $F_2CC_6H_4CF_2$.

High-temperature vacuum pyrolysis (700–950°C) of dihalides [136,137] and disulphones of the type [136,137],



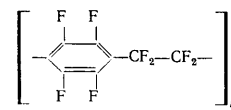
where $n = 1$ or 2, X = Cl, Br, or SO_2R (R is a small alkyl group), and R′ = H, Cl, or C_6H_5, and also of the cyclic dimer of $\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene [136,138],



has been recently used successfully in the synthesis of poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoro-*p*-xylylenes. Strong transparent sheets have been obtained by this method from the disulphones and the dimer.

Poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene (m.p. about 500°C) is a highly crystalline insoluble polymer with a very high thermal stability; the mechanical properties of sheets of this polymer hardly change on heating in air for 3000 h at 250°C or 100 h at 300°C.

A method for the preparation of polyperfluoro-*p*-xylylene from the corresponding disulphone has also been patented [137]:



---o0o---

The new field of the chemistry of organofluorine compounds (polycondensation fluoropolymers) discussed in the present review is at present in the stage of establishment and development, the number of studies in this field increasing continuously: for example three-quarters of the relevant studies were published in the 1960's.

The interest in polycondensation fluoropolymers can be readily understood: in almost every class materials have been found with promising operational properties (high thermal stability, chemical stability, elasticity at low temperatures, etc.). Thus polyperfluoroalkylenetriazines have the highest thermal stability among the known elastomers, poly(hexafluoropentylene adipate) has found application in the preparation of special oil- and frost-resistant rubber, fluorine-containing polyurethanes based on polyperfluoroethers can be used as elastomers at low temperatures, etc.

At the same time one should note that the introduction of fluorine atoms does not always lead to the improvement of the properties of the polymer and in some cases a decrease of thermal and chemical stability, for example, has been observed as a function of the structure of the polymer. Unfortunately exhaustive data on the properties of polycondensation fluoropolymers are frequently lacking in the literature and therefore it is difficult to make a comparative analysis of fluoropolymers and their non-fluorinated analogues. Whenever possible, such a comparison has been made in the appropriate places in the text.

Polycondensation reactions of fluorine-containing compounds frequently lead to polymers with a lower molecular weight compared with their non-fluorinated analogues. This is due to the powerful electron-accepting influence of the fluorine atoms on the reactivity of the functional

groups. Recently definite progress has been achieved in the synthesis of polycondensation fluoropolymers—high-molecular-weight compounds of various classes which were previously regarded as unattainable—had been synthesised. Their synthesis became possible owing to the application of new methods of polycondensation and also the use of new types of fluorine-containing monomers.

The entire accumulated experience on the synthesis of fluoropolymers and the study of their properties show that further studies in this interesting series of still new polymers are justified.

REFERENCES

1. I. L. Knunyants, Chih-Yuan Li, and V. V. Shokina, Uspekhi Khim., 32, 1053 (1963) [Russ. Chem. Rev., No. 9 (1963)].
2. R. Guenthner, US P. 2 606 206 (1952); Chem. Abs., 46, 10 979 (1952).
3. R. Filler, J.O'Brien, J. Tenner, and M. Hauptschein, J. Amer. Chem. Soc., 75, 966 (1953).
4. M. Hauptschein, C. Stokes, and E. Nodiff, J. Amer. Chem. Soc., 74, 4005 (1952).
5. R. Herbst and B. Landrum, US P. 2 842 524 (1958); Chem. Abs., 52, 17 797 (1958).
6. G. Schweiker and P. Robitschek, J. Polymer Sci., 24, 33 (1957).
7. G. Schweiker and P. Robitschek, US P. 3 016 361 (1962); Chem. Abs., 56, 7480 (1962).
8. M. Hauptschein, J. O'Brien, C. Stokes, and R. Filler, J. Amer. Chem. Soc., 75, 87 (1953).
9. M. Fein and E. O'Brien, US P. 3 332 902 (1967); Chem. Abs., 68, 50 809 (1968).
10. G. Schweiker and P. Robitschek, US P. 3 016 360 (1962); Chem. Abs., 56, 7480 (1962).
11. W. Severson, US P. 3 240 800 (1966).
12. E. Gouinlock, J. Verbanic, and G. Schweiker, J. Appl. Polymer Sci., 1, 361 (1959).
13. I. M. Dolgopol'skii, Kh. A. Dobina, V. S. Fikhtengol'ts, S. A. Kamysheva, M. I. Sinaiskaya, P. T. Balashova, and R. V. Zolotareva, Vysokomol. Soed., 9A, 1536 (1967).
14. I. Ya. Poddubnyi, E. G. Erenburg, and G. G. Kartasheva, Symposium, "Geterotsepnye Vysokomolekulyarnye Soedineniya" (Heterochain Macromolecular Compounds), Izd. Nauka, Moscow, 1963, p. 3.
15. C. A. Barson and C. R. Patrick, Uspekhi Khim., 33, 977 (1964) [Russ. Chem. Rev., No. 8 (1964)].
16. L. Wall and S. Straus, J. Res. Nat. Bur. Stand., 65A, 227 (1961).
17. J. M. Cox, B. A. Wright, and W. W. Wright, J. Appl. Polymer Sci., 8, 2935 (1964).
18. F. Trischler and J. Hollander, J. Polymer Sci., 7, A1, 971 (1969).
19. B. P. 798 824 (1958); Chem. Abs., 53, 2685 (1959).
20. R. C. Evers and G. F. Ehlers, J. Polymer Sci., 7, A1, 3021 (1969).
21. D. Jaquiss, US P. 3 220 978 (1965).
22. A. Ya. Yakubovich, I. L. Knunyants, E. M. Gromban, I. L. Maslennikova, N. P. Gambaryan, and G. Yh. Gordon, USSR P. 132 403 (1960); Ref. Zhur. Khim., 24P, 222 (1961).
23. V. V. Korshak, S. V. Vinogradova, and V. A. Pankratov, Dokl. Akad. Nauk SSSR, 156, 880 (1964).
24. S. S. Karapetyan, A. Ya. Yakubovich, and I. L. Knunyants, Vysokomol. Soed., 6, 1550 (1964).
25. V. V. Korshak, S. V. Vinogradova, and V. A. Pankratov, Vysokomol. Soed., 7, 1689 (1965).
26. V. V. Korshak, S. V. Vinogradova, and V. A. Pankratov, Izv. Akad. Nauk SSSR, Ser. Khim., 1649 (1965).
27. V. V. Korshak, I. F. Manucharova, S. V. Vinogradova, and V. A. Pankratov, Vysokomol. Soed.,
28. V. V. Korshak, I. L. Knunyants, S. V. Vinogradova, N. P. Gambaryan, V. A. Pankratov, and B. R. Lifshits, USSR P. 170 662 (1965); Byul. Izobret., No. 9, 67 (1965).
29. Chem. Proces., 30, 77 (1967).
30. I. L. Knunyants, Ch'in-Yun Ch'ên, N. P. Gambaryan, and E. M. Rokhlin, Zhur. Vses. Khim. Obshch. im Mendeleeva, 5, 114 (1960).
31. M. D. Bargamova, Yu. A. Cheburkov, and I. L. Knunyants, USSR P. 138 037 (1961); Ref. Zhur. Khim., 11P 191 (1962).
32. V. V. Rode, Symposium, "Novye Polikondensatsionnye Polimery" (New Polycondensation Polymers) (Edited by Z. A. Rogovin), Izd. Mir, Moscow, 1969, p. 229.
33. J. Critchley, V. McLoughlin, J. Thrower, and M. White, Chem. Ind. (London), 934 (1969).
34. W. Cummings and E. Lynch, BP. 1 079 516 (1967); Chem. Abs., 67, 82 566 (1967).
35. V. N. Odinokov, Candidates Thesis, Institute of General Chemistry, USSR Academy of Sciences, Novosibirsk, 1966.
36. S. Evans and E. Lynch, BP. 1 141 719 (1969); Chem. Abs., 70, 78 572 (1969).
37. W. Rausher and U. Tucker, J. Amer. Chem. Soc., 76, 3599 (1954).
38. L. Allewelt, US P. 2 570 180 (1951); Chem. Abs., 46, 50 810 (1952).
39. E. Fear, J. Thrower, and J. Veitsch, J. Appl. Chem., 5, 589 (1955).
40. R. S. Muromova, G. V. Demidova, and G. B. Ovakimyan, Vysokomol. Soed., 6, 1145 (1964).
41. B. Marks and G. Schweiker, J. Polymer Sci., 43, 229 (1960).
42. I. L. Knunyants, Chih-Yuan Li, and V. V. Shchokina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1461 (1961).
43. Chih-Yuan Li, Candidate's Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1961.
44. L. B. Sokolov, "Polikondensatsionnyi Metod Sinteza Polimerov" (The Polycondensation Method for the Synthesis of Polymers), Izd. Khimiya, Moscow, 1966, p. 227.
45. L. B. Sokolov, Vysokomol. Soed., 6, 2117 (1964).
46. L. B. Sokolov, A. S. Astakhova, and L. A. Ryzhova, USSR P. 169 248 (1965); Ref. Zhur. Khim., 7S 291P (1966).
47. A. Ya. Yakubovich and R. M. Gitina, Vysokomol. Soed., 8, 1137 (1966).
48. A. Ya. Yakubovich, R. M. Gitina, A. M. Simonov, and G. S. Markova, Vysokomol Soed., 10A, 2172 (1968).
49. R. M. Gitina, I. E. Kardash, G. I. Braz, A. Ya. Ardashnikov, A. N. Pravednikov, and A. Ya. Yakubovich, Vysokomol. Soed., 9B, 447 (1967).
50. D. F. Sokolova and L. B. Sokolov, Vysokomol. Soed., 10B, 407 (1968).
51. B. F. Malichenko, Candidate's Thesis, Institute of General Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1964.
52. S. Kwolek, US P. 3 328 352 (1967); Chem. Abs., 68, 60 466 (1968).
53. I. L. Knunyants, S. V. Vinogradova, and B. R. Livshits, USSR P. 226 845 (1968); Byul. Izobret., No. 29, 73 (1968).

54. R. Dine-Hart and W. Wright, J. Appl. Polymer Sci., 11, 609 (1967).
55. B. F. Malichenko and I. M. Sopina, Vysokomol. Soed., 10B, 468 (1968).
56. E. L. Zaitseva, R. M. Gitina, and A. Ya. Yakubovich, Vysokomol. Soed., 9B, 498 (1967).
57. A. Ya. Yakubovich, R. M. Gitina, E. L. Zaitseva, G. S. Markova, and A. P. Simonov, Vysokomol. Soed., 12A, 2520 (1970).
58. J. Critchley, J. Pippett, and M. White, "Tezisy 5 Mezhdunarodnogo Simpoziuma po Khimii Ftora" (Abstracts of Reports at the Fifth International Symposium on the Chemistry of Fluorine) (Translated into Russian), Moscow, 1969, p. 108.
59. J. M. Barton and J. P. Critchley, Polymer, 11, 212 (1970).
60. F. Rogers, French P. 1 399 078 (1965).
61. H. Brown, Amer. Chem. Soc. Polymer Preprints, 5, 243 (1964).
62. H. Brown, Encycl. Polym. Sci. Technol., 7, 179 (1967).
63. B. R. Livshits, G. Kh. Dymshits, I. L. Knunyants, and S. V. Vinogradova, USSR P. 230 416 (1968); Byul. Izobret., No. 34, 89 (1968).
64. B. P. 960 140 (1964); Chem. Abs., 61, 13 450 (1964).
65. B. P. 797 795 (1958); Chem. Abs., 53, 1830 (1959).
66. J. Hollander, F. Trischler, and R. Gosnell, Amer. Chem. Soc. Polymer. Preprints, 7, 1086 (1966).
67. J. Hollander, F. Trischler, and R. Gosnell, J. Polymer Sci., 5, A1, 2757 (1967).
68. B. F. Malichenko, E. V. Shelud'ko, and Yu. Yu. Kercha, Vysokomol. Soed., 9A, 2482 (1967).
69. B. F. Malichenko and E. V. Shelud'ko, Vysokomol. Soed., 10B, 395 (1965).
70. J. Hollander, F. Trischler, and E. Harrison, Amer. Chem. Soc. Polymer Preprints, 8, 1149 (1967).
71. R. Gosnell and J. Hollander, J. Macromol. Sci. Phys., 1B, 831 (1967).
72. F. Trischler, US P. 3 463 762 (1969); Chem. Abs., 71, 82 091 (1969).
73. F. Trischler and J. Hollander, US P. 3 463 761 (1969); Chem. Abs., 71, 82 193 (1969).
74. P. Tarrant and E. Stamp, Zhur. Vses. Khim. Obshch. im Mendeleeva, 15, 34 (1970).
75. P. Morgan, US P. 3 373 139 (1968).
76. H. Brown, Rubber World, 139, 408 (1958).
77. H. Brown, J. Polymer Sci., 44, 9 (1960).
78. M. P. Krasuskaya and I. L. Knunyants, USSR P. 145 748 (1961); Byul. Izobret., No. 6, 51 (1962).
79. H. Brown, US P. 3 086 946 (1963); Chem. Abs., 59, 9813 (1963).
80. Chem. Week, 94, 35 (1964).
81. L. Wall, W. Pummer, and S. Straus, Rubber World, 139, 407 (1958).
82. S. L. Madorsky, "Thermal Degradation of Organic Polymers" (Translated into Russian), Izd. Mir, Moscow, 1967, p. 167.
83. I. E. Kardash, A. Ya. Ardashnikov, and A. N. Pravednikov, Vysokomol. Soed., 9A, 1081 (1967).
84. W. Johnson, Rubber World, 161, 79 (1970).
85. E. L. Zaitseva, G. I. Braz, A. Ya. Yakubovich, V. P. Bazov, R. M. Gitina, L. G. Petrova, and I. M. Filatova, Zhur. Fiz. Khim. Obshch. im Mendeleeva, 8, 353 (1963).
86. E. L. Zaitseva, R. M. Gitina, A. Ya. Yakubovich, G. I. Braz, L. G. Petrova, and V. P. Bazov, Zhur. Obshch. Khim., 34, 2816 (1964).
87. A. Ya. Yakubovich, E. L. Zaitseva, R. M. Gitina, V. P. Bazov, I. M. Filatova, and G. I. Braz, Zhur. Obshch. Khim., 36, 862 (1966).
88. H. Brown and C. Wetzel, J. Org. Chem., 30, 3724 (1965).
89. J. Johns, Amer. Chem. Soc. Polymer Preprints, 5, 239 (1964).
90. E. Dorfman and W. Emerson, French P. 1 560 303 (1969); Chem. Abs., 71, 125 482 (1969).
91. Chem. Week blad., 99, 121 (1966).
92. W. Emerson and E. Dorfman, French P. 1 554 658 (1969); Chem. Abs., 71, 49 988 (1969).
93. C. Fritz and J. Warnell, US P. 3 317 484 (1967); Chem. Abs., 67, 22 455 (1967).
94. C. Fritz and J. Warnell, US P. 3 347 901 (1967); Chem. Abs., 68, 13 703 (1968).
95. E. Dorfman and C. Bean, US P. 3 354 204 (1967); Chem. Abs., 68, 13 594 (1968).
96. E. Dorfman, W. Emerson, R. Carr, and C. Bean, Rubber Chem. and Technol., 39, 1175 (1966).
97. W. Griffin, Rubber Chem. and Technol., 39, 1178 (1966).
98. W. Griffin, US P. 3 369 002 (1968).
99. G. Grindahl, W. Bajzer, and O. Pierce, J. Org. Chem., 32, 603 (1967).
100. B. P. 1 114 198 (1968); Chem. Abs., 69, 19 823 (1968).
101. H. Brown, M. Cheng, L. Parcell, and D. Pilipovich, J. Org. Chem., 26, 4407 (1961).
102. B. P. 988 119 (1965); Chem. Abs., 63, 700 (1965).
103. L. Plummer and C. Marvel, J. Polymer Sci., 2AI, 2559 (1964).
104. A. Ya. Yakubovich, G. G. Rozantsev, G. I. Braz, and V. P. Bazov, Vysokomol. Soed., 6, 838 (1964).
105. V. V. Korshak, T. M. Frunze, V. V. Kurashev, and G. P. Lopatina, Vysokomol. Soed., 6, 1251 (1964).
106. D. Burmeister, M. Sander, and K. Bergert, Macromol. Chem., 89, 199 (1965).
107. G. I. Braz, I. E. Kardash, V. V. Kopylov, A. F. Oleinik, G. G. Ryazantsev, A. N. Pravednikov, and A. Ya. Yakubovich, Khim. Geterotsikl. Soed., 339 (1968).
108. R. M. Gitina, G. I. Braz, V. P. Bazov, A. Ya. Yakubovich, Vysokomol. Soed., 8, 1535 (1966).
109. E. L. Zaitseva, R. M. Gitina, and A. Ya. Yakubovich, see Ref. 58, p. 110.
110. W. Cummings and E. Lynch, B. P. 1 077 243 (1967).
111. H. Fielding, B. P. 1 085 882 (1967); Chem. Abs., 67, 117 564 (1967).
112. M. Hellman, A. Bibbo, and W. Pummer, J. Amer. Chem. Soc., 77, 3650 (1955).
113. H. Fielding, B. P. 1 052 482 (1966).
114. W. Pummer and J. Antonucci, Amer. Chem. Soc. Polymer Preprints, 7, 1071 (1966).
115. J. Cotter, J. Lancaster, and W. Wright, Amer. Chem. Soc. Polymer Preprints, 5, 474 (1964).
116. G. Brooke, R. Chambers, J. Heyes, and W. Musgrave, J. Chem. Soc., 731 (1964).
117. E. Parfitt and J. Thrower, B. P. 1 100 261 (1968); Chem. Abs., 68, 59 245 (1968).
118. J. Thrower and M. White, Amer. Chem. Soc. Polymer Preprints, 7, 1076 (1966).
119. J. Wright and H. Fielding, B. P. 1 004 636 (1965).
120. W. Pummer and L. Wall, Sci. Tech. Aerospace Rept., 3, 1400 (1965); Chem. Abs., 65, 7279 (1966).
121. J. Coffer, G. Knight, J. Lancaster, and W. Wright, J. Appl. Polymer Sci., 12, 2481 (1968).
122. W. Pummer and L. Wall, Science, 127, 643 (1958).
123. W. Pummer and L. Wall, J. Res. Nat. Bur. Stand., 68A, 277 (1964).

124. R. N. Johnson, A. G. Farnham, R. O. Clendinning, W. F. Hale, and C. N. Merriam, J. Polymer Sci., 5, A1, 2375 (1967).
125. P. Robson, M. Stacey, R. Stephens, J. Tatlow, J. Chem. Soc., 4754 (1960).
126. N. Christopher, J. Cotter, and G. Knight, J. Appl. Polymer Sci., 12, 863 (1968).
127. R. Jones, J. Amer. Chem. Soc., 69, 2346 (1947).
128. J. Antonucci and L. Wall, J. Res. Nat. Bur. Stand., 71A, 33 (1967).
129. J. Birchall and R. Haszeldine, J. Chem. Soc., 3719 (1961).
130. R. Haszeldine and J. Birchall, B. P. 990 980 (1965).
131. L. Wall and J. Antonucci, US P. 3 394 190 (1968).
132. V. McLoughlin and J. Thrower, Chem. Ind. (London), 1557 (1964).
133. H. Smith, US P. 3 397 118 (1968).
134. W. Hertler, J. Org. Chem., 28, 2877 (1963).
135. S. Show, B. P. 1 074 708 (1965); Chem. Abs., 68, 3368 (1968).
136. S. Show, W. Loeb, and C. White, J. Appl. Polymer Sci., 13, 2325 (1969).
137. S. Show, French P. 1 395 586 (1962); Chem. Abs., 63, 18 295 (1965).
138. S. Show, B. P. 3 268 599 (1966); Chem. Abs., 66, 11 327 (1967).

Karpov Physicochemical Institute,
Moscow