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Hexafluoroisopropylidene-containing Polyheteroarylenes

V.V.Korshak, I.L.Knunyants, A.L.Rusanov, and B.R.Livshits

The methods of synthesis of various condensation monomers containing the hexafluoroisopropylidene groups and the polyheteroarylenes based on them are examined. The influence of the hexafluoroisopropylidene groups incorporated in the main chains of the macromolecules is analysed and it is shown that polyheteroarylenes containing these are characterised by an improved solubility and fire resistance and that the articles based on them have a higher elasticity.
The bibliography includes 88 references.

CONTENTS

I. Introduction 288
II. Condensation monomers containing hexafluoroisopropylidene groups 288
III. Polyheteroarylenes containing hexafluoroisopropylidene groups in the main chains of the macromolecules 290

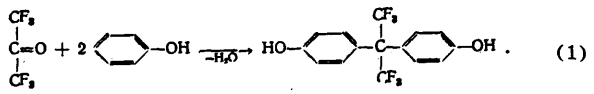
I. INTRODUCTION

Halogen and in particular fluorine-containing condensation polymers have attracted much attention by investigators in the course of the last 25 years. A series of monographs and careful reviews,[1-5] indicating the enormous variety of the halogen-containing polymers synthesised and their properties, have been devoted to the principal advances in this field. Among the numerous fluorine-containing polymers, aromatic polycondensation systems are of special interest[1-3] and among them those where the fluorine atoms are located in the side chains and not in the benzene ring.[3] Typical representatives of such polymers are polycondensates containing hexafluoroisopropylidene groups. A systematic analysis of the advances in this field is not available in the literature. For this reason, the selected subject of this review is an examination of the advances in the synthesis and investigation of condensation monomers and polyheteroarylenes containing hexafluoroisopropylidene groups.

II. CONDENSATION MONOMERS CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS

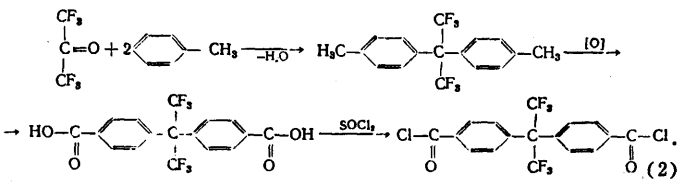
The synthesis of condensation monomers containing hexafluoroisopropylidene groups is based on the reactions of hexafluoroacetone with various aromatic compounds containing mobile hydrogen atoms[6-11] and the subsequent reaction of the simplest condensation products.[7-18]

Thus Knunyants and co-workers[16] achieved the condensation of hexafluoroacetone with phenol in the presence of anhydrous HF, which resulted in the formation of 2,2-di(*p*-hydroxyphenyl)hexafluoropropane produced at the present time in considerable amounts and known under the name "bisphenol AF":[11]



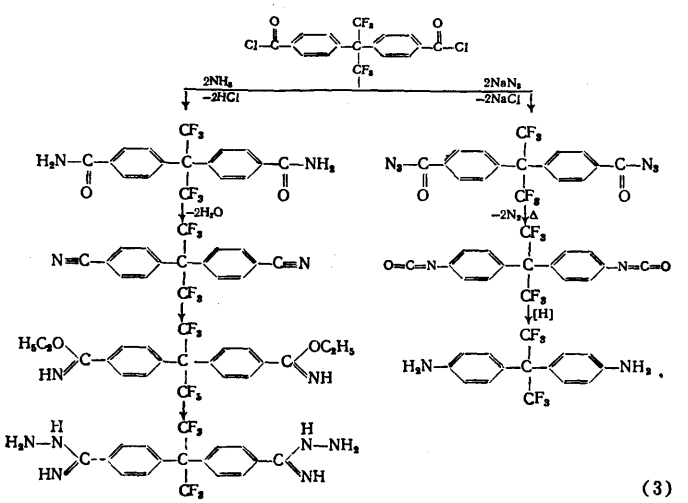
(1)

The development of this approach to the synthesis of bifunctional derivatives of 2,2-diarylhexafluoropropane led to the formation of a whole series of compounds with hexafluoroisopropylidene groups,[7-10] which are of independent interest as monomers for polycondensation or serving as intermediates in the synthesis of condensation monomers with a complex structure. In particular, a dicarboxylic acid and acid dichloride derived from 2,2-diarylhexafluoropropane have been obtained by condensing hexafluoroacetone with toluene and subsequent reactions of 2,2-di(4-tolyl)hexafluoropropane:[7-10]



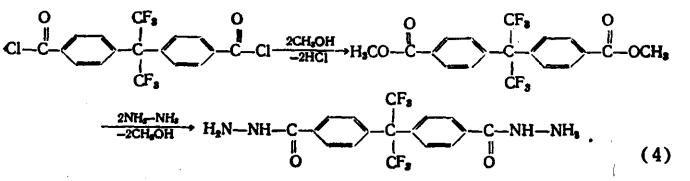
(2)

Subsequent reactions of the dichloride of 2,2-di(*p*-carboxyphenyl)hexafluoropropane led to the formation of the corresponding diamide, diazide, diisocyanate, and diamine[7-9] as well as the dinitrile, the diethyl bis(iminoester), and the bisamidrazone of 2,2-di(*p*-carboxyphenyl)hexafluoropropane:



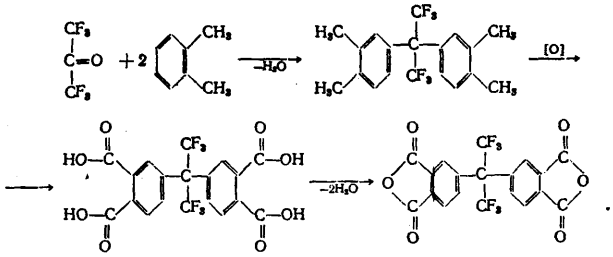
(3)

Subsequently the diphenyl ester, the dimethyl ester, and the dihydrazide of 2,2-di(*p*-carboxyphenyl)hexafluoropropane were synthesised:[8]



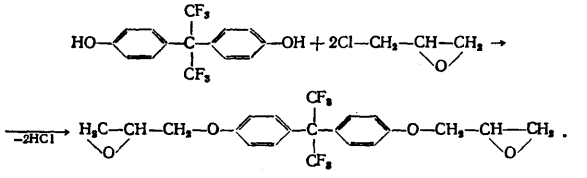
(4)

2,2-Di(3,4-dimethylphenyl)hexafluoropropane, whose oxidation yielded 2,2-di(3,4-dicarboxyphenyl)hexafluoropropane, dehydrated subsequently to the corresponding dianhydride, was obtained by the reaction of hexafluoroacetone with *o*-xylene:[9]



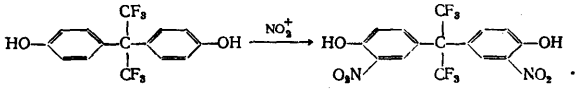
(5)

Evidently the final products and the series of intermediates indicated in Schemes (1)–(5) refer to the majority of the classes of monomers used in polycondensation reactions.[12] On the other hand, many of them have been used in various reactions leading to new monomers. 2,2-Di(4-hydroxyphenyl)-hexafluoropropane is used particularly vigorously for this purpose. Thus the di(4-glycidyl) ether of 2,2-di(4-hydrophenyl)hexafluoropropane has been synthesised by its interaction with epichlorohydrin:[13,19]



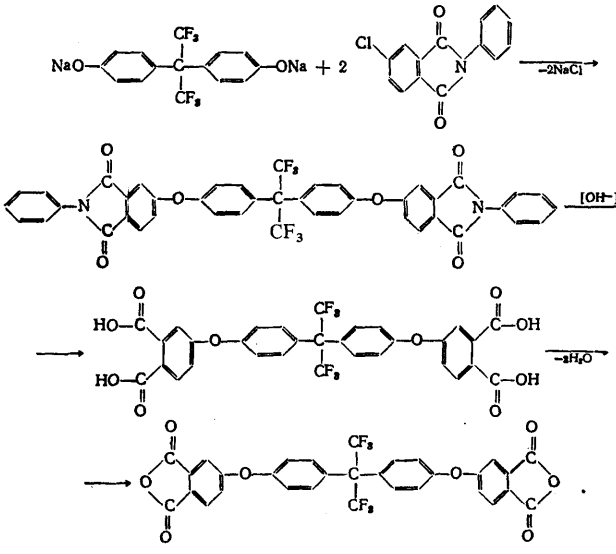
(6)

The nitration of this bisphenol yielded 2,2-di(4-hydroxy-3-nitrophenyl)hexafluoropropane:[14]



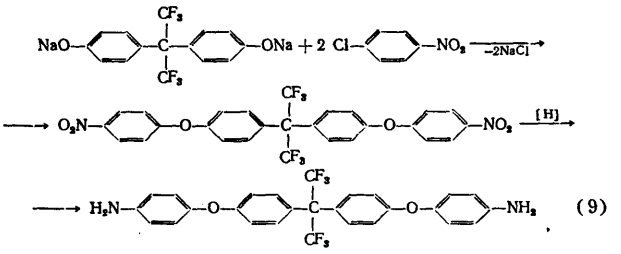
(7)

The reaction of its disodium salt with 4-chloro-*N*-phenylphthalimide and subsequent reactions of the latter afforded the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)phenyl]-hexafluoropropane:[15,16]



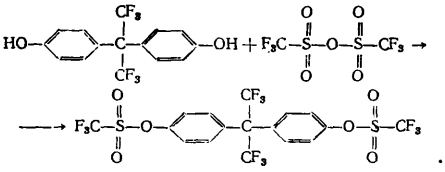
(8)

The interaction of the same diphenoxide with twice the molar amount of *p*-chloronitrobenzene made it possible to obtain 2,2-di[4-(4-nitrophenoxy)phenyl]hexafluoropropane, which was subsequently reduced to 2,2-di[4-(4-aminophenoxy)phenyl]hexafluoropropane:[18]



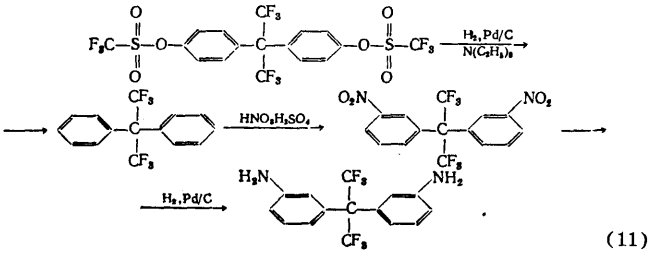
(9)

A considerable amount of hexafluoroisopropylidene-containing monomers have been synthesised[11] from 2,2-di(4-trifluoromethanesulphonyloxyphenyl)hexafluoropropane, obtained by treating bisphenol AF with trifluoromethanesulphonic (triflic) anhydride:[20,21]



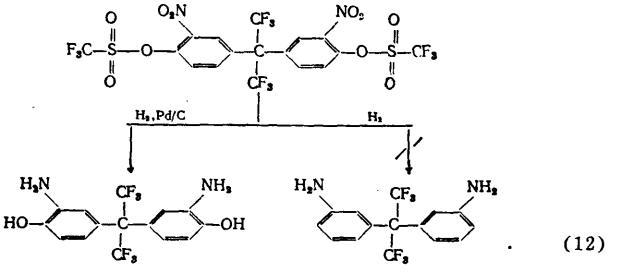
(10)

The ditriflate obtained in this way was reduced catalytically over palladium on charcoal in the presence of triethylamine. This resulted in the formation of 2,2-diphenylhexafluoropropane, whose nitration and subsequent reduction afforded 2,2-di(3-aminophenyl)hexafluoropropane:[11]



(11)

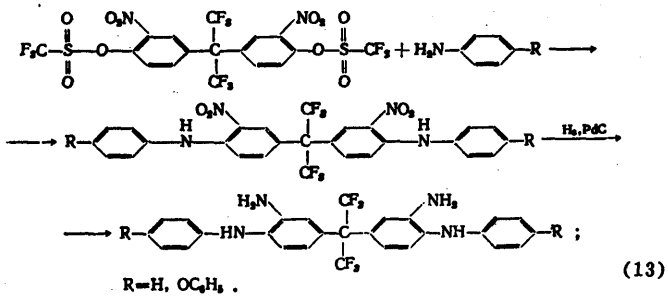
The nitration of the ditriflate gave rise to 2,2-di(3-nitro-4-trifluoromethane-sulphonyloxyphenyl)hexafluoropropane, whose hydration led to the formation of 2,2-di(3-amino-4-hydroxyphenyl)hexafluoropropane instead of the expected 2,2-di(3-aminophenyl)hexafluoropropane:[11]



(12)

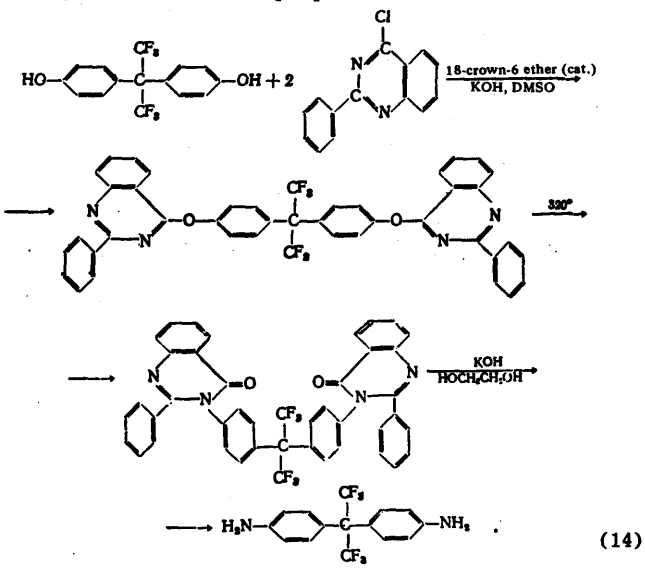
We may note that the former product can apparently be obtained also by a simple procedure via the nitration of bisphenol AF[14] and the reduction of the resulting 2,2-di(4-hydroxy-3-nitrophenyl)hexafluoropropane.

The replacement of the triflate group in 2,2-di(3-nitro-4-trifluoromethane-sulphonyloxyphenyl)hexafluoropropane by aromatic amines with subsequent reduction of the reaction product led to the formation of various 2,2-di(3-amino-4-arylamino)hexafluoropropanes:[11]



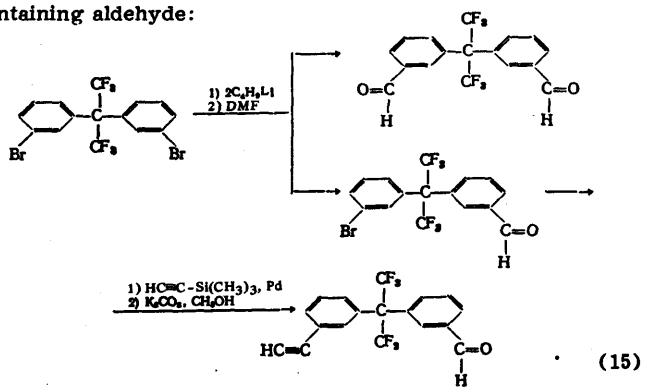
R=H, OC_6H_5 . (13)

Finally bisphenol AF has been converted[11] into 2,2-di(4-aminophenyl)hexafluoropropane. A method, which is general for the conversion of phenols and bisphenols into amines and diamines, was used for this purpose:



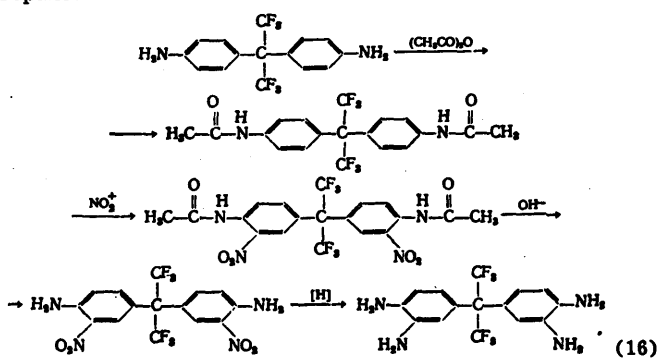
(14)

New monomers have been obtained via a series of reactions also from the isomeric hexafluoroisopropylidene-containing aromatic diamines. Thus 2,2-di(3-aminophenyl)hexafluoropropane was converted via the Sandmeyer reaction into 2,2-di(3-bromophenyl)hexafluoropropane,[11] which was in its turn converted by treatment with organolithium compounds into 2,2-di(3-formylphenyl)- and 2-(3-bromophenyl)2-(3-formylphenyl)hexafluoropropanes and further into an ethynyl-containing aldehyde:



(15)

The corresponding bis(*o*-phenylenediamine) has been obtained from 2,2-di(4-aminophenyl)hexafluoropropane via stages involving the acetylation of the amino-groups, nitration, the removal of the acyl protecting group, and reduction of the resulting 2,2-di(4-amino-3-nitrophenyl)hexafluoropropane:[9]

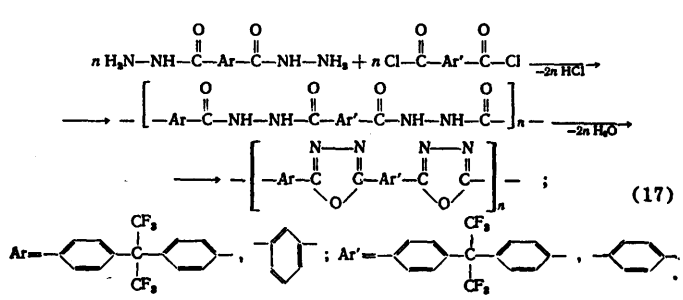


(16)

The simplest monomers containing hexafluoroisopropylidene groups were used successfully at the beginning of the 1960's for the synthesis of heterochain polymers—polyesters,[23] polycarbonates,[23,24] polyarylates,[25] polyamides,[26] polyurethanes,[8] etc. In these and later[27] studies it was already shown that the trifluoromethyl groups as side substituents at the central carbon atom significantly improve the mechanical properties of the polymers and sharply increase their solubility in any solvent, improving thereby their capacity for being worked and converted into articles. Since the capacity for being converted into articles and the deformation-strength characteristics of the latter are in fact the weak features of many polyheteroarylenes,[28] it appeared entirely natural to synthesize polyheteroarylenes containing hexafluoroisopropylidene groups in order to modify the properties of these systems in the required direction.

III. POLYHETEROARYLENES CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS IN THE MAIN CHAINS OF THE MACROMOLECULES

One of the first polyheteroarylenes which have attracted the attention of investigators as regards their modification by hexafluoroisopropylidene groups were poly-1,3,4-oxadiazoles.[27,29] These polymers were synthesised using a traditional approach,[30,31] via the interaction of the dihydrazide and (or) dichloride of 2,2-di(*p*-carboxyphenyl)hexafluoropropane with monomers of the dihydrazide and acid dichloride series with subsequent thermal cyclisation of the resulting polyhydrazides:[27,29]

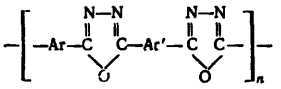


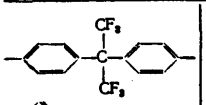
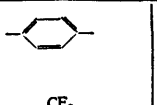
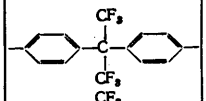
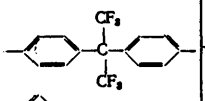
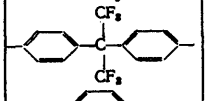
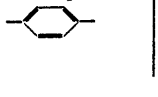
(17)

Certain characteristics of the poly-1,3,4-oxadiazoles synthesised in this way are presented in Table 1.

Analysis of the data in Table 1 indicates a significant (~50 °C) decrease of the softening temperature of the polyoxadiazoles on passing from the structure lacking hexafluoroisopropylidene groups to one containing the maximum number of the latter. On the other hand, the solubility of poly-1,3,4-oxadiazoles increases with increase of the content of fluorine atoms in the polymer. Polymers based on the dichloride of 2,2-di(*p*-carboxyphenyl)hexafluoropropane and its dihydrazide are the most soluble.[27] The tendency of the fluorine-containing polymers to dissolve can be accounted for, according to Livshits et al.,[27] both by the affinity of the trifluoromethyl groups for polar solvents and by the non-rigid structure of these polymers as a consequence of the presence in them of bulky groups facilitating the diffusion of the solvent.

Table 1. Certain characteristics of poly-1,3,4-oxadiazoles having the general formula[27,29]



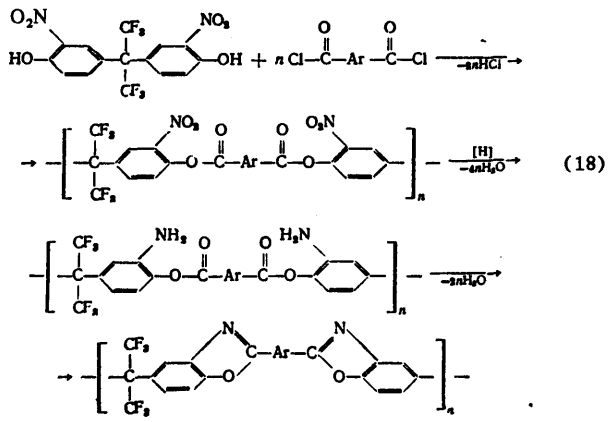
Ar	Ar'	T^{*}_{soft}	Solubility**			
			nitrobenzene	TCE:phenol (3:1)	DMF	DMSO
		370	∓	∓	+	∓
		360	∓	+	+	∓
		330	+	+	+	+
		380	–	–	–	–

*Here and henceforth the softening temperature T_{soft} is assumed to be the value obtained from the thermomechanical curves.

**Here and henceforth the following notation has been adopted in designating solubilities: +—soluble in the cold, ±—soluble on heating, ∓—swells, – —insoluble.

It is noteworthy that the data presented in Table 1 refer to polymers obtained by thermal solid-phase polycyclisation (at 275 °C for 20 h). It might have been expected that catalytic cyclisation in solution would lead to the formation of polymers with a still higher solubility. Overall, poly-1,3,4-oxadiazoles containing hexafluoroisopropylidene groups are promising polymers and, provided that the problem of the starting materials can be solved successfully, they may be of significant practical interest.

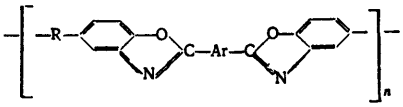
The synthesis of polybenzoxazoles containing hexafluoroisopropylidene groups has also attracted much attention by investigators. These polymers have been obtained by the reductive polyheterocyclisation reaction[14,32] in accordance with the scheme[14,32–34]

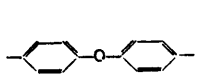
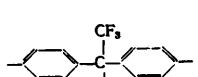
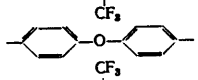
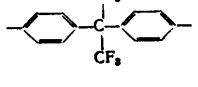
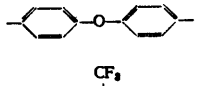
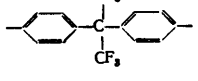


(18)

The synthesis in *N*-methyl-2-pyrrolidinone (N-MP) using reduced iron and HCl, which play simultaneously the role of a reductant and the cyclisation catalyst, led to the formation of high-molecular-weight polymers characterised by high degrees of cyclisation. Certain characteristics of the polybenzoxazoles synthesised are presented in Table 2.

Table 2. Certain characteristics of polybenzoxazoles having the general formula[14]



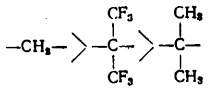
R	Ar	η^{*}_{int}, dl g^{-1}	T^{**}_{soft}, °C	T_{decomp}, °C	Solubility	
					TCE:phenol (3:1)	N-MP
		1.20	260–270	400	+	–
		1.32	250–260	360	+	+
		1.48	280–290	435	+	–
		1.37	280–270	410	+	–
		0.82	270–280	420	+	+
		1.08	240–250	370	+	+

*The intrinsic viscosity (η_{int}) was determined in a 3:1 TCE–phenol mixture at 25 °C.

**Here and henceforth the decomposition temperature (T_{decomp}) was assumed to be the temperature at which 10% of the mass was lost under the conditions of dynamic TGA (in air, $\Delta T = 4.5$ K min^{-1}).

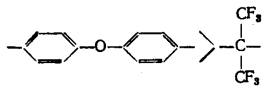
Analysis of the data in Table 2 indicates the relation between the structure and properties of the polymers, which is identical with that found for poly-1,3,4-oxadiazoles (Table 1): the replacement of the traditional aromatic "bridging" groups by hexafluoroisopropylidene fragments leads to the improvement of the solubility of the polymers and at the same time to a decrease of the softening temperatures, the combination of the two factors improving the capacity of polybenzoxazoles for being worked.

Data on the thermal stability of the polyheteroarylenes synthesised have attracted attention. Despite the rather arbitrary nature of the data obtained under the conditions of dynamic thermogravimetric analysis (DTA) thermal stability series are quite clearly manifested: in relation to the "bridging" groups R, series have the following form:



(19)

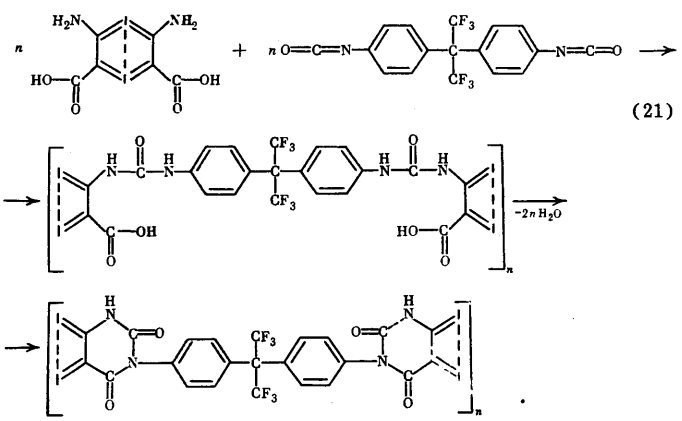
while in relation to dicarboxylic acid residues Ar it is



(20)

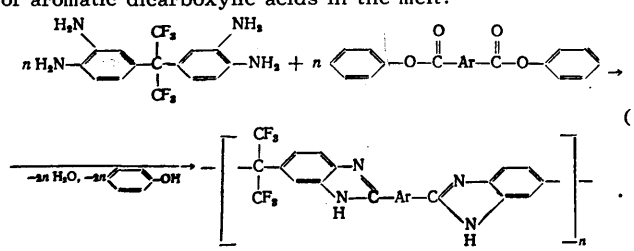
The data obtained agree both with the results of a study[23] where it was claimed that the thermal stability of the polycarbonate based on 2,2-di(4-hydroxyphenyl)hexafluoropropane is greater than that of the polycarbonate based on bisphenol A and with the results of an investigation[27] in which a reduced thermal stability of polyheteroarylenes containing hexafluoroisopropylidene groups was claimed.

The data on the synthesis of polyquinazolinediones[35] and polybenzimidazoles[36] containing hexafluoroisopropylidene groups appear to be somewhat less systematic. Polyquinazolinediones containing hexafluoroisopropylidene groups have been obtained by the reaction of bis(anthranilic acids) with 2,2-di(4-isocyanatophenyl)hexafluoropropane:[35]



(21)

Polybenzimidazoles containing hexafluoroisopropylidene groups have been obtained by the reaction of 2,2-di(3,4-diaminophenyl)hexafluoropropane with the diphenyl esters of aromatic dicarboxylic acids in the melt:[36]



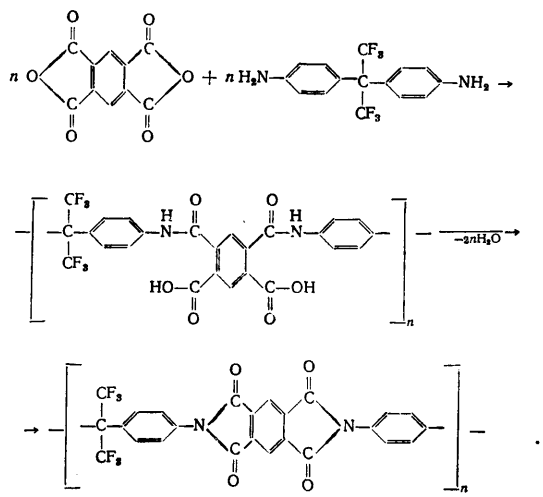
(22)

In all cases the introduction of hexafluoroisopropylidene groups led to the changes in the properties of polymers noted above and in addition to an appreciable increase of their fire resistance. The latter factor is extremely important in view of the considerable interest in fire resistant polymers.[37] Almost all investigators are unanimous in claiming a positive influence of the trifluoromethyl groups on the fire resistance of polymers, but in most cases the results obtained are qualitative rather than quantitative, which naturally hinders the analysis of the dependence of this property of the polymers on the structure.

As can be seen from the foregoing, the modification of the properties of polymers by hexafluoroisopropylidene groups concerned many classes of polyheteroarylenes but polyimides have attracted most attention by investigators.[30,38] This can be explained to a considerable extent by the special place which polyimides occupy among polyheteroarylenes and also by the extensive possibilities for the modification of their structure by hexafluoroisopropylidene groups.

It is noteworthy that analysis of the "structure–properties" and especially "structure–solubility" relations is very difficult precisely for polyimides owing to the differences between the methods of their synthesis (thermal cyclisation of polyamidoacids or catalytic cyclisation of prepolymers in solution), the differences between their viscosity characteristics, etc.

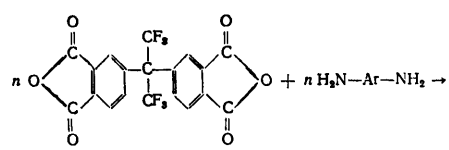
One of the first attempts at the modification of polyimides by hexafluoroisopropylidene groups concerns the synthesis of polypyromellitimide from 2,2-di(4-aminophenyl)hexafluoropropane[27] by a two-stage method:

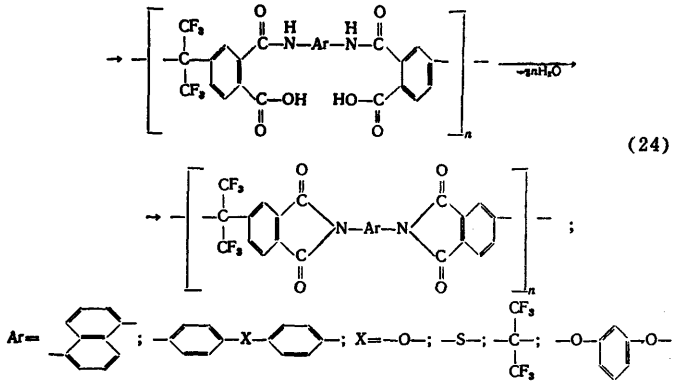


(23)

The polyimides obtained proved to be insoluble in organic solvents.

According to a series of data,[39–43] the polyimides based on the dianhydride of 2,2-di(3,4-dicarboxyphenyl)hexafluoropropane (dianhydride 6F) and various diamines are also soluble only in $SbCl_3$. They were obtained by a two stage method in accordance with the scheme

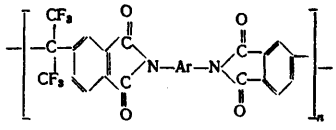


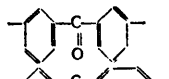
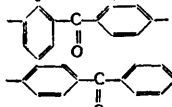
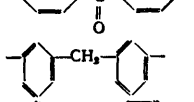
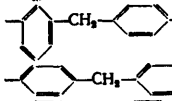
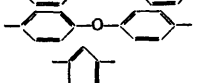
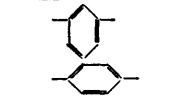
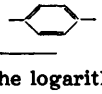


(24)

On the other hand, according to Clair et al.,[17] the polyimides containing hexafluoroisopropylidene groups are characterised in many instances by a satisfactory solubility in dipolar aprotic solvents (Table 3).

Table 3. Certain characteristics of polyimides having the general formula[17]

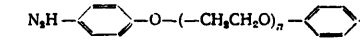


Ar	η_{log}*	T_{soft}, °C	Solubility			
			N-MP	DMA	DMF	*m*-cresol
	0.47	260	+	÷	+	±
	0.25	288	+	+	+	−
	0.35	311	−	−	−	−
	1.23	248	+	+	+	±
	0.86	272	−	−	−	−
	1.82	290	−	−	−	−
	2.20	307	−	±	+	+
	0.54	303	+	+	+	+
	0.90	339	+	÷	+	+

*The logarithmic viscosity (η_{log}) was determined in N-MP at 25 °C.

In the search for ways of increasing the solubility of the imides, investigators turned to the use of a diamine and a dianhydride containing in their molecules a combination of one hexafluoroisopropylidene group and two ether linkages, namely 2,2-di[(4-aminophenoxy)phenyl]hexafluoropropane[18] and the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)-phenyl]hexafluoropropane.[15,16,44-46] However, a significant increase of the solubility of the required polyimides could not be achieved by this procedure. Furthermore, an extremely detailed analysis of the relation between the structure of the polyimides based on asymmetric diamines and their solubility[17,47] showed that the polymers based on dianhydride 6F are much more soluble than the polyimides based on the same diamines and the dianhydride of 2,2-di[4-(3,4-dicarboxy-phenoxy)phenyl]hexafluoropropane.[17] This at first sight anomalous phenomenon is probably associated with the greater content of hexafluoroisopropylidene units per conventional unit length of the macromolecule in polyimides based on dianhydride 6F. Certain characteristics of the polyimides based on dianhydride 6F and aromatic diamines with symmetrical and asymmetrical structures are listed in Table 3. In the analysis of the data in Table 3, the somewhat unexpected higher solubility of the polyimide based on dianhydride 6F and *p*-phenylenediamine compared with the polyimides based on dianhydride 6F and diamines such as 4,4'-diaminobenzophenone, di(4-aminophenyl)methane, and di(4-aminophenyl)-ether has attracted attention. By analogy with the above, the explanation of the observed phenomenon is probably the greater number of hexafluoroisopropylidene units per conventional unit length of the macromolecule of the polyimide based on *p*-phenylenediamine.

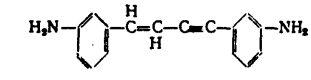
Together with the traditional aromatic amines, systems with a more specific structure have been used in the synthesis of polyimides based on dianhydride 6F. The interaction of dianhydride 6F with diamines containing oligo-oxymethylene groups, having the general formula



(25)

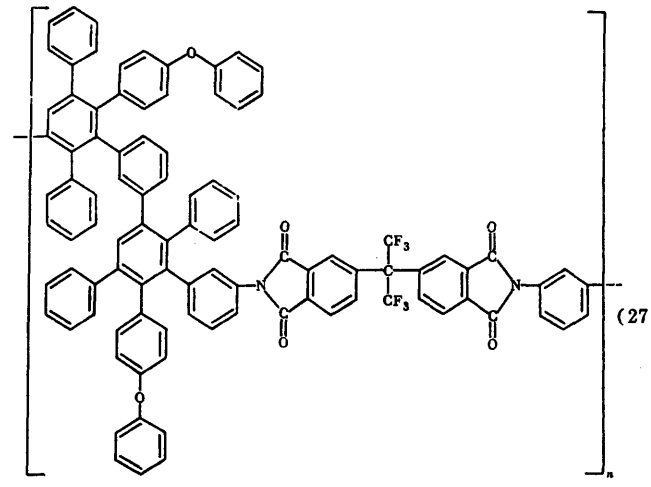
(n = 1,2,3,4), in *m*-cresol at 165–180 °C yielded polyimides which are soluble in chloroform and soften at 135–255 °C, depending on the structure of the diamine.[48,49]

A polyimide soluble in chloroform and dimethylacetamide (DMA) has been obtained under analogous conditions from dianhydride 6F and (*E*)-3,3'-(but-1-en-3-ynylene)dianiline:[44-46]



(26)

A polyimide having the formula



(27)

containing, together with hexafluoroisopropylidene groups, also 4-phenoxyphenyl and phenyl side groups which impart an improved solubility to rigid-chain monomers,[51] has been obtained[50] from dianhydride 6F. This polyimide is characterised by a glass point of 240 °C, is soluble in aromatic,

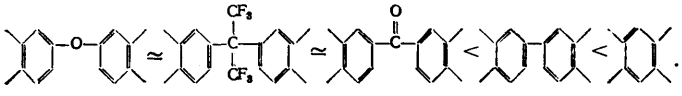
chlorinated, and polar aprotic solvents, and retains 80% of its initial mass on thermal ageing at 343 °C for 200 h.[50]

The comparatively low softening temperatures of hexafluoroisopropylidene-containing polyimides make it possible to obtain from the low-molecular-weight polymers of this class articles with effective physicomechanical properties by cast moulding or extrusion.[42,52,53] The most promising polymers of this type—systems based on dianhydride 6F and aromatic diamines—are used by the Dupont Company as a basis for the development of binding or reinforced plastics[54–59] known by the name NR-150. According to Gibbs and Breder,[54] polyimides based on dianhydride 6F and various aromatic diamines are obtained by the chemical cyclisation of poly(*o*-carboxy)amides. The polymers obtained are soluble in pyridine, N-MP, and DMF. The glass points of the polyimides are in the range 229–385 °C, depending on the structure of the diamines. A low content of cavities (~1%) in the final materials is achieved by pressing at temperatures exceeding the glass points of the polyimides. Analogous pressing conditions are a precondition for success in the separation of glass plastics from solutions of poly(*o*-carboxy)amides. In all cases the presence of hexafluoroisopropylidene groups prevents the crystallisation of the polyimides. Glass plastics based on NR-150 have a tensile strength up to 3500 kg cm^{-2}, a modulus of elasticity of 2.24×10^5 kgf cm^{-2}, a static bending strength of 4900 kgf cm^{-2}, and a shear strength of 660 kgf cm^{-2}.[59] The most heat resistant of these systems can be used at 342 °C[54] and they retain 80% of their initial strength characteristics after ageing at 260 °C for 5000 h.[59]

Experiments with various polyimide binders have shown that NR-150 has the highest thermal stability and is most suitable for prolonged use in outer space.[59] Together with their employment as binders, such polyimide systems are of interest as adhesives and coatings.[60]

The positive effect of hexafluoroisopropylidene groups on the solubility of polyimides has been demonstrated also in relation to cardo-copolyimides with various microstructures synthesised using dianhydride 6F[61,62] and 2,2-di(4-aminophenyl)hexafluoropropane among various monomers.[62,63]

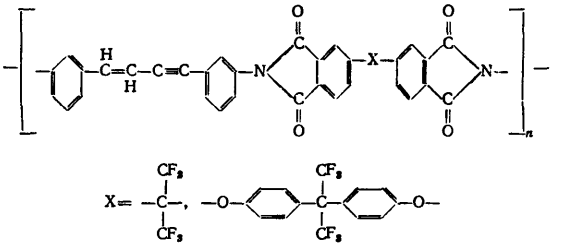
Comprehensive investigation of the properties of the copolyimides synthesised has shown that the introduction of hexafluoroisopropylidene groups tends to increase the solubility of the copolyimides. In terms of their influence on the softening temperatures of the polymers, the dianhydrides of tetracarboxylic acids can be arranged in the following sequence:[62]



(28)

The unique capacity of hexafluoroisopropylidene-containing oligo- and poly-heteroarylenes for being worked made them useful as thermoreactive polymeric systems. In recent years this field, which reduces to the creation of readily worked systems which are hardened after conversion into articles, has become one of the dominant fields in the chemistry of thermostable polymers. In particular, oligomers and polymers with ethynyl groups,[64] capable of cyclotrimerising with formation of trisubstituted phenyl intermolecular units, have attracted much attention. The ethynyl groups can be located in the main chains of the macromolecules, in the side substituents, and in the end groups of the oligo- and polyheteroarylenes. The use of reactive solvents and plasticisers, containing ethynyl groups and capable of participating, on hardening, in the formation of three-dimensional structures, proved to be extremely effective in a number of instances.

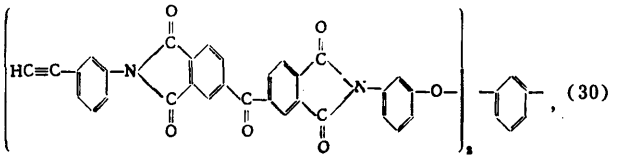
Each of the approaches enumerated above has been applied to some extent to hexafluoroisopropylidene-containing systems. Thus the introduction of ethynyl groups into the main chain of the macromolecule has been achieved in the synthesis of enyne polyimides:[44–46]



(29)

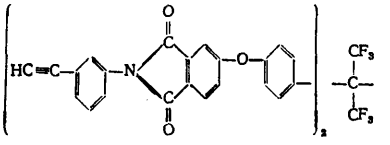
The hardening of these polymers at 265–316 °C led to the formation of "cross-linked" three-dimensional systems.

In order to make it easier to convert into finished articles the imidised oligomer Therimid-600, having the structural formula



(30)

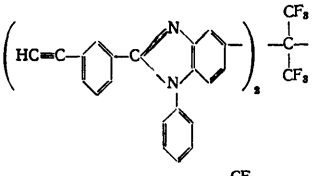
use was made of the reactive plasticiser



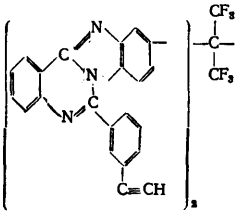
(31)

obtained by the reaction of the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane [Scheme (8)] with 3-ethynylaniline.[64]

Finally, bis(*N*-phenylbenzimidazole)[65] and bisbenzimidazoquinazoline[66] with ethynyl end groups, i.e.



(32)



(33)

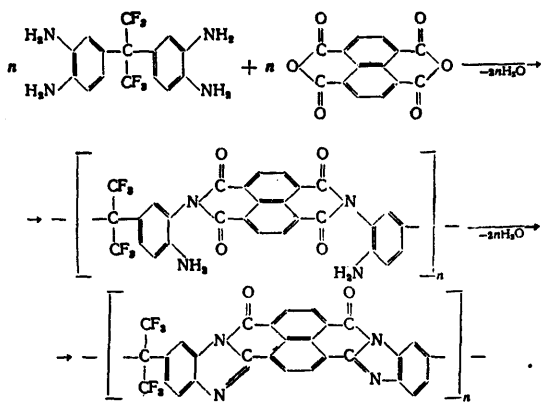
were converted into thermostable three-dimensional products by thermal polycyclotrimerisation.[64]

The extremely successful use of hexafluoroisopropylidene groups for the improvement of the "workability" of the traditional polyheteroarylenes led Korshak and co-workers to take the next step, namely to attempt the modification of "ladder" polyheteroarylenes by hexafluoroisopropylidene groups. The choice of these systems was dictated by the fact

that many ladder systems have high thermal stabilities and heat resistances but are extremely difficult to work with and to convert into articles.[67-71]

The hexafluoroisopropylidene-containing ladder polyheteroarylenes were investigated within the framework of the synthesis of polynaphthoyleneazoles, namely polynaphthoylenebenzimidazoles and polynaphthoylene-*sym*-triazoles, which are the products of the three-stage reactions of bis(naphthalic anhydrides) with tetrafunctional aromatic nucleophiles [bis(*o*-phenylenediamine) and bisamidrazones of dicarboxylic acids][67] and also polybenzimidazoquinazolines and polybenzo(dipyrimidobenzimidazoles), which were obtained in two stages, by the reaction of diamines, containing benzimidazole rings in the *o*-positions relative to the amino-groups, with derivatives of aromatic dicarboxylic acids.[69-71]

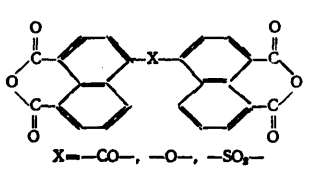
In the course of studies on hexafluoroisopropylidene-containing polynaphthoylenebenzimidazoles, a polymer was developed on the basis of 2,2-di(3,4-diaminophenyl)hexafluoropropane and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[72-75] It was synthesised in accordance with the scheme



(34)

The reaction was carried out in phenolic solvents—*m*-cresol and phenol—using benzoic acid as the catalyst.[76] This made it possible to synthesise the polymer under comparatively mild conditions (at 180 °C). The reaction, occurring under homogeneous conditions, led to the formation of high-molecular-weight polynaphthoylenebenzimidazole with a degree of cyclisation close to 100%.[72-75] The polymer obtained dissolves not only in acid but also in phenolic solvents (*m*-cresol and a mixture of phenol and tetrachloroethane). Films with a tensile strength of 980 kg cm^{-2} at 25 °C and a 60% elongation on rupture, retaining satisfactory deformation-strength characteristics up to 380 °C, have been obtained from such solutions by casting.

In order to increase further the solubility of polynaphthoylenebenzimidazoles, the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid was replaced in reaction (33) by the dianhydrides of carbonyl-, oxy-, and sulphonyl-bis(naphthalic acids):[77-82]



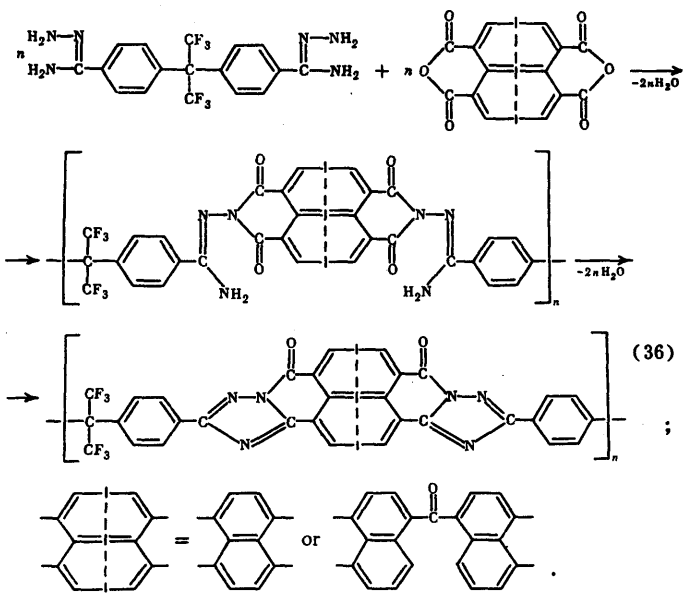
X=—CO—, —O—, —SO$_2$—

(35)

The resulting polynaphthoylenebenzimidazoles, containing alternating hexafluoroisopropylidene and other "bridging" groups, dissolve not only in phenolic solvents but also in hot N-MP. However, one should note that these polymers had very low viscosities ($\eta_{int} \approx 0.3$ dl g^{-1}), which precludes unambiguous conclusions about the influence of their structure on the solubility.

Overall, polynaphthoylenebenzimidazoles with hexafluoroisopropylidene groups, in the first place the polymer based on 2,2-di(3,4-diaminophenyl)hexafluoropropane and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid, are of undoubted interest and, provided that the problem of the starting materials can be solved, their use may extend outside the framework of academic research.

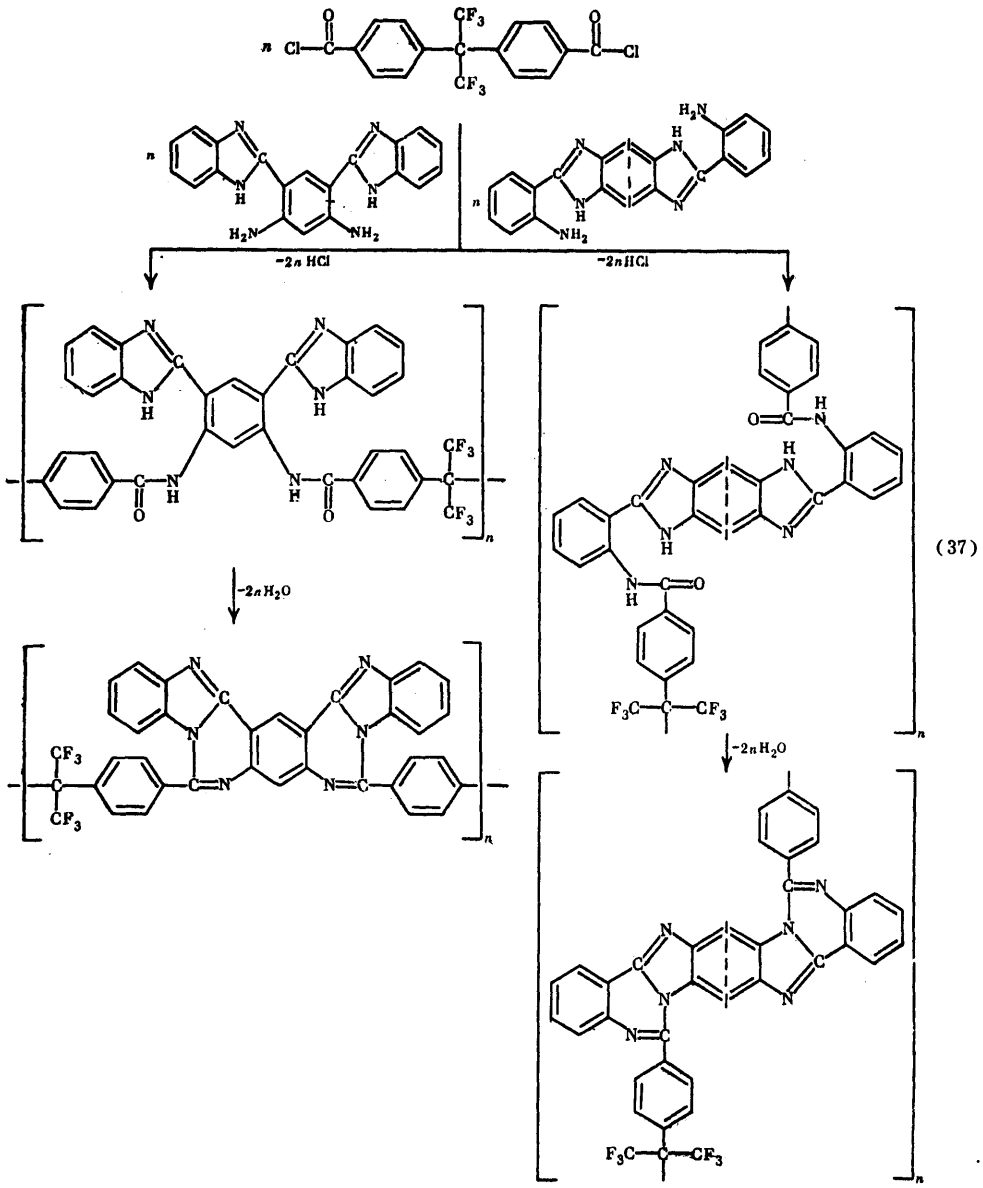
Together with polynaphthoylenebenzimidazoles, polynaphthoylene-*sym*-triazoles, which are the products of the interaction of the bisamidrazone of 2,2-di(*p*-carboxyphenyl)hexafluoropropane with bis(naphthalic anhydrides), attracted the attention of the same group of investigators:[83,84]



(36)

Polynaphthoylene-*sym*-triazoles were synthesised[83,84] under conditions identical to those used to obtain polynaphthoylenebenzimidazoles; high-molecular-weight polymers soluble in phenolic solvents and having softening temperatures in the range 380–420 °C with oxygen indices of 43–46 were obtained.

In order to synthesise polybenzimidazoquinazolines and polybenzo[di(pyrimidobenzimidazoles)] containing hexafluoroisopropylidene groups,[85-88] bis[2(2-aminophenyl)6-benzimidazoles] and 1,3-di(2-benzimidazolyl)-4,6-diaminobenzenes were made to react with the dichloride of 2,2-di(*p*-carboxyphenyl)hexafluoropropane [Scheme (37)].



(37)

The reactions were carried out under the conditions of a two-stage process; the first stage was performed at room temperature in N-MP in hexamethylphosphoramide and the second in the solid phase at 350–380 °C. The resulting polybenzimidazoquinazolines and polybenzo[di(pyrimidobenzimidazoles)] dissolved only in H_2SO_4 and CF_3COOH, but it is not clear whether this is a consequence of the severe conditions in the cyclisation processes or of the chemical structure of the polymers.

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Analysis of the data presented in the review shows that the introduction of hexafluoroisopropylidene groups into the main chains of the macromolecules constitutes an effective method of imparting an improved solubility, an improved fire resistance, and also elasticity to rigid-chain polymers. Provided that the starting materials can be obtained, this field may prove to be promising for the preparation of polymers with a valuable set of properties.

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