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Synthesis and Properties of Fluorine-Containing Aromatic Condensation Polymers Obtained from Bisphenol AF and Its Derivatives

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9.1. INTRODUCTION

Fluorine-containing polymers exhibit unique chemical and physical properties and high performance that are not observed with other organic polymers. They possess high thermal stability, high chemical stability, a low coefficient of friction, low adhesion, water and oil repellency, low refractive index, and outstanding electric insulation. In addition, there have recently been new expectations of selective permeability, piezoelectricity, and biocompatibility.

These characteristics of fluorine-containing polymers are imparted by the highest electronegativity (4.0), the third smallest van der Waals radius (0,135 nm), and low polarizability ($\alpha = 1.27 \times 10^{-24}$ cm^3) of the fluorine atom, strong bonding energy (472 kJ/mol) and small atomic distance (0.138nm) of the C—F bond, and the weak intermolecular cohesive energy of the polymer.

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Research on fluorine-containing condensation polymers is rather limited compared to that on fluorine-containing addition polymers. This fact is attributed to the difficulty in synthesis and the high cost of fluorine-containing condensation monomers. Recently, 2,2-bis(4-hydroxyhpenyl)-1, 1,1,3,3,3-hexafluoropropane (Bisphenol AF) with a hexafluoroisopropylidene unit, $HOC_6H_4C(CF_3)_2$-C_6H_4OH, was produced commercially from hexafluoroacetone and phenol, and now Bisphenol AF and its derivatives are available as condensation monomers.

Replacement of isopropylidene units in polymer backbones by units of hexafluoroisopropylidene is known to enhance solubility, water and oil repellency, thermal stability, and glass transition temperature (T_g) and to decrease crystallinity and water absorption.[1]

This chapter deals with the synthesis and properties of fluorine-containing condensation polymers from Bishpenol AF and its derivatives. Much of the work reported has been conducted in our laboratory. An extensive review has already been published by Cassidy and co-workers[1] on the synthesis of fluorine-containing condensation polymers.

9.2. POLY(CARBONATE)S

9.2.1. Synthesis

A fluorine-containing poly(carbonate) was first synthesized by Knunyants and co-workers from Bisphenol AF and phosgene.[2] However, detailed properties of this polymer other than the softening temperature of 170°C have not been reported.

Commerical poly(carbonate)s have been produced mainly through a low-temperature solution polycondensation of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) using phosgene as a carbonylation agent.[3] However, phosgene vapor is extremely toxic, and the preparation using phosgene is not usually suitable for a laboratory-scale synthesis of poly(carbonate)s. Disphosgene (trichloromethyl chloroformate), a liquid, and triphosgene [bis-(trichloromethyl)-carbonate], a solid, react similarly to phosgene as carbonylation agents but can be handled more easily and safely than phosgene.

It has been reported that high-molecular-weight poly(carbonate)s can be synthesized using *N,N'*-carbonyldiimidazole as a condensing agent under mild conditions.[4,5] However, the reagent is very sensitive to moisture and must be handled with extreme care.

Bisphenol-AF-derived poly(carbonate) **(2)** has been synthesized by the two-phase transfer-catalyzed polycondensation of Bisphenol AF **(1)** with trichloromethyl chloroformate (TCF) in organic-solvent–aqueous-alkaline solution systems with a variety of quaternary ammonium salts at room temperature (Scheme 1).[6]
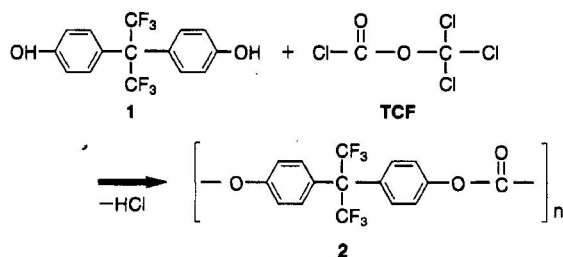
Scheme 1

The following quaternary ammonium salts are used as phase transfer catalyst: *tetra-n*-butylammonium chloride (TBAC), *tetru-n*-butylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC), and benzyltriethylammonium bromide (BTEAB). Chlorinated hydrocarbons, such as dichloromethane (DCM), chloroform (CF), tetrachloromethane (TCM), 1,2-dichloromethane (DCE), and nitrobenzene (NB) are used as solvents. The effects of phase-transfer catalyst and solvent on the yield and reduced viscosity are summarized in Table 9.1.

When TBAB is used as a phase-transfer catalyst, sodium hydroxide as a base, and DCE as a solvent, both the molecular weight and yield of the poly(carbonate) are relatively high. Bisphenol AF-derived poly(carbonate) **(2)** having reduced viscosity of 0.35 dl/g is obtained in a 84% yield at ambient temperature under the

Table 9.1. Effects of Phase-Transfer Catalyst and Organic Solvent on the Yield and Reduced Viscosity of Bisphenol-AF-Derived Poly(Carbonate)[6]

| No.	Reaction conditions		Polymer	
	Catalyst	Solvent	Yield (%)	η_{red} (dl/g)
1	TBAB	DCM	13	0.41
2	TBAB	CF	74	0.30
3	TBAB	TCM	83	0.14
4	TBAB	DCE	84	0.35
5[a]	TBAB	DCE	87	0.05
6[b]	TBAB	DCE	66	0.05
7[c]	TBAB	DCE	71	0.37
8	TBAB	NB	76	0.37
9	TBAC	DCM	84	0.25
10	BTEAB	DCM	60	0.13
11	BTEAC	DCM	63	0.35

[a] 5.00 mol of TCF was used.
[b] 14.3 mol NaOH was used.
[c] KOH (28.5 mmol) was used instead of NaOH.

optimum reaction conditions, in which 7.50 mmol of Bisphenol AF is reacted with 7.50 mmol of TCF using 3.15 mmol of TBAB, 30 ml of 1 M aqueous sodium hydroxide and 37.5 ml of DCE. Although polymers with slightly higher molecular weights are obtained using DCM and NB as organic solvents, the yields are lower. This rather lower molecular weight of Bisphenol AF poly(carbonate) **(2)** compared to Bisphenol A-derived poly(carbonate) **(3)** is attributed to trifluoromethyl groups having a higher electron-withdrawing property than methyl groups, which cause a decrease in reactivity of phenolic hydroxyl groups.

Random copoly(carbonate)s **(5)** are obtained by the reaction of mixtures of Bisphenol AF **(1)** and Bisphenol A **(4)** with TCF (Scheme 2).[6]
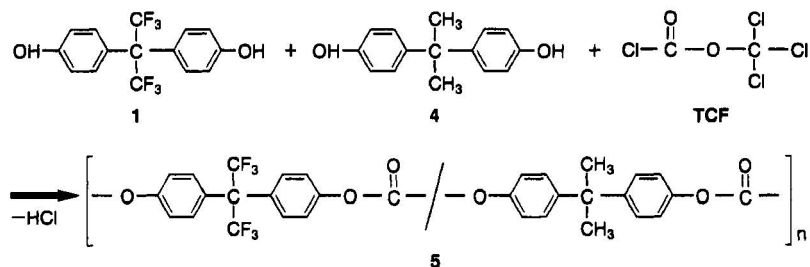
Scheme 2

Table 9.2 shows the results of a preparation of a series of copoly(carbonate)s having a wide range of hexafluoroisopropylidene unit content. Reduced viscosity of copoly(carbonate)s **(5)** decreases gradually with increasing feed ratio of Bisphenol AF **(1)** to Bisphenol A **(4).** This is attributed to the lower nucleophilicity of Bisphenol AF induced by strongly electron-withdrawing trifluoromethyl groups as described above.

Table 9.2. Preparation of Fluorine-Containing
Poly(Carbonate)s[6]

Bisphenol AF/Bisphenol A (unit ratio)		Yield (%)	η_{red} (dl/g)
Feed	Polymer		
100/0	100/0	84	0.35
80/20	81/19	79	0.19
60/40	54/46	81	0.27
50/50	47/53	80	0.28
40/60	41/59	85	0.51
20/80	19/81	75	0.54
0/100	0/100	85	0.73

9.2.2. Properties

Aromatic poly(carbonate) from 2,2-bis(4-hydrozyphenyl)propane (Bisphenol A) and phosgene is utilized as one of the high-performance engineering thermoplastics and finds versatile applications owing to its excellent characteristics, including high thermal stability, high impact strength, high refractive index, high transparency, and self-extinguishing property.

The solubility and thermal stability of polymers are usually improved and the surface energy is decreased by substituting fluorine atoms for the hydrogen atoms in the isopropylidene units connecting phenylene units in the main chain.

It has been determined from X-ray diffraction measurements that poly(carbonate)s containing Bisphenol AF moiety are all amorphous.[6] The (T_g) of poly(carbonate)s increases with an increase in hexafluoroisopropylidene unit from 149°C for Bisphenol A poly(carbonate) (**3**) to 169°C for Bisphenol AF poly(carbonate) (**2**) (Table 9.3).[6] Thermooxidative stability is also improved by the introduction of fluorine atoms into the isopropylidene units. The 10% weight-loss temperature (DT_{10}) increases from 429 to 460°C and the residual weight (RW) at 500°C goes from 37 to 57% by perfluorination of the isopropylidene units.

The solubility is generally improved by the introduction of fluorine atoms into aromatic condensation polymers. Poly(carbonate)s containing hexafluoroisopropylidene units are much more soluble than Bisphenol A poly(carbonate) (**3**). All of the hexafluoroisopropylidene-unit-containing poly(carbonate)s become soluble in acetone, ethyl acetate, chloroform, and dimethyl sulfoxide (DMSO) in addition to the solvents of Bisphenol A poly(carbonate) (**3**). Colorless, transparent, and flexible films are prepared from hexafluoroisopropylidene-unit-containing poly(carbonate)s by casting or pressing.

The contact angle (θ) by water at 25°C in air is 84° for Bisphenol A poly(carbonate) (**3**) film (Table 9.4).[6] Introduction of 19% of Bisphenol AF unit increases the value of (θ) to 90° and from that point is almost constant irrespective of fluorine content. This abrupt increase in (θ) is attributed to the migration and

Table 9.3. Thermal Properties of Fluorine-Containing Poly(Carbonate)s[6]

Bisphenol AF/Bisphenol A (unit ratio)	T_g (°C)	DT_{10} (°C)	RW (%)
100/0	169	460	51
81/19	163	442	48
54/46	160	431	50
47/53	158	436	48
41/59	156	439	41
19/81	152	434	45
0/100	149	429	37

Table 9.4. Water Contact Angle of Fluorine-Containing
Poly(Carbonate)s[6]

Bisphenol AF/Bisphenol A (unit ratio)	θ_w (degree)
100/0	91
81/19	91
54/46	92
41/53	91
41/59	91
19/81	90
0/100	84

concentration of trifluoromethyl groups to the surface of the polymer film owing to their lower surface energy as observed by ESCA.[7] The critical surface tension of Bisphenol AF poly(carbonate) (**2**) is determined to be 20 mN/m at 25°C from the Zisman plot using n-butanol–water mixtures as wetting liquids.[6] This value is much lower than the 45 mN/m at 25°C reported for Bisphenol A poly(carbonate) (**30**).[8]

The high refractive index of Bisphenol A poly(carbonate) (**3**) is decreased by the incorporation of the Bisphenol AF moiety. The refractive index of Bisphenol A poly(carbonate) (**3**) is 1.585,[9] whereas that of Bisphenol AF poly(carbonate)s (**2**) is 1.426. Poly(carbonate)s containing a small amount of Bisphenol AF moiety can be used as sheaths of optical fibers of Bisphenol A poly(carbonate) (**3**).

The tensile strength and tensile modulus decrease and the elongation increases by the introduction of fluorine atoms into isopropylidene units of Bisphenol A poly(carbonate) (**3**),[6] i.e., poly(carbonate) becomes more flexible by the introduction of hexafluoroisopropylidene units. The increased flexibility is attributed to the weaker intermolecular interaction induced by fluorine atoms.

9.3. POLY(FORMAL)S

9.3.1. Synthesis

Hay *et al.*[10,11] have prepared high-molecular-weight a Bisphenol-A-derived poly(formal) (**6**) using a phase-transfer catalyst in DCM. A Bisphenol-AF-derived poly(formal) (**7**) is also synthesized by solution polycondensation of Bisphenol AF (**1**) with DCM in highly polar cosolvents in the presence of potassium hydroyxide (Scheme 3).[12] Aprotic polar solvents such as *N,N*-dimethylformamide

(DMF), *N,N*-dimethylacetamide (DMAc), DMSO, hexamethylphosphoric tria-mide (HMPA), and *N*-methyl-2-pyrrolidone (NMP) may be used as cosolvents.
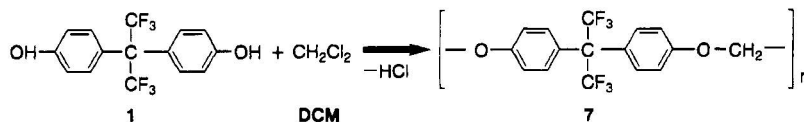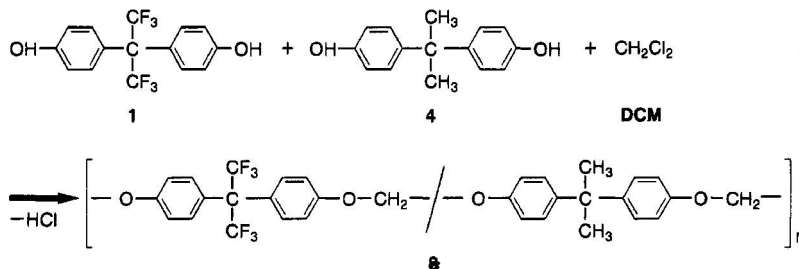

Scheme 3

A large excess of DCM to Bisphenol AF (**1**) is required for production of high-molecular-weight Bisphenol A poly(formal) (**7**) because DCM acts as the reactant as well as the cosolvent. The most suitable molar amount of DCM is about 12 times that of Bisphenol AF (**1**).

The effects of cosolvents on the reduced viscosity and yield are summarized in Table 9.5. DMAc and NMP lead to the formation of high-molecular-weight Bisphenol AF poly(formal) (**7**) in a high yield. The optimum reaction conditions are 48 mmol of DCM, 14 mmol of potassium hydroxide, and 5 ml of NMP for 5 mmol of Bisphenol AF, resulting in the formation of Bisphenol AF poly(formal) (**7**) with reduced viscosity of 4.62 dl/g in a 87% yield at 75°C.[12]

Fluorine-containing copoly(formal)s (**8**) are synthesized in a similar manner by reacting the mixtures of Bisphenol AF (**1**) and Bisphenol A (**4**) with DCM (Scheme 4).[12]

Scheme 4

Copoly(formal)s (**8**) with high reduced viscosities are readily obtained in high yields irrespective of the feed ratio of Bisphenol AF (**1**) and Bisphenol A (**4**) (Table 9.6).

9.3.2. Properties

Bisphenol-A-derived poly(formal) (**6**) shows poor solubility and is only soluble in dichloromethane, chloroform, THF, HMPA, and NMP. However, poly(formal)s containing the Bisphenol AF moiety are easily soluble in a wide variety of organic solvents, such as acetone, ethyl acetate, benzene, toluene,

Table 9.5. Effect of Cosolvent on the Yield and Reduced
Viscosity of Bisphenol-AF-Derived Poly(Formal)[12]

	Polymer	
Solvent	Yield (%)	η_{red} (dl/g)
DMF	49	0.11
DMAc	89	4.40
DMSO	92	1.96
HMPA	92	1.40
NMP	87	4.62

m-cresol, and most aprotic polar solvents in addition to the solvents for Bisphenol
A poly(formal) (**6**).[12]

Resistance to acids is improved by the introduction of fluorine atoms.
Bisphenol A poly(formal) (**6**) decomposes rapidly with significant coloration in
strong acids, whereas Bisphenol AF poly(formal) (**7**) is stable in concentrated
sulfuric acid.[12]

Poly(formal)s containing Bisphenol AF moiety are all amorphous.[12] The T_g
is 88°C for Bisphenol A poly(formal) (**6**) increases with increasing Bisphenol AF
content, and rises to 123°C for Bisphenol AF poly(formal) (**7**) (Table 9.7).[12]

The thermooxidative stability is improved by increasing the hexafluoroiso-
propylidene unit content.[12] The DT_{10} in air is raised from 363°C for Bisphenol A
poly(formal) (**6**) to 398°C for Bisphenol AF poly(formal) (**7**), and the RW at
500°C is increased from 48 to 73%.[12]

A contact angle by water is 86° for Bisphenol A poly(formal) (**6**), is
increased to 93° by the introduction of 28 mol% of hexafluoroisopropylidene
unit, and then becomes almost constant irrespective of fluorine content.[12] As

Table 9.6. Preparation of Fluorine-Containing
Poly(Formal)s[12]

Bisphenol AF/Bisphenol A (unit ratio)			
Feed	Polymer	Yield (%)	η_{red} (dl/g)
100/0	100/0	87	4.62
75/25	75/25	90	1.44
50/50	52/48	88	2.05
25/75	28/72	91	5.31
0/100	0/100	92	3.54

Table 9.7. Thermal Properties of Fluorine-Containing Poly(Formal)s[12]

Bisphenol AF/Bisphenol A (unit ratio)	T_g (°C)	DT_{10} (°C)	RW (%)
100/0	123	398	73
75/25	114	389	60
52/48	108	375	60
28/72	100	359	56
0/100	88	363	48

observed for poly(carbonate)s, this is attributed to the concentration of hydrophobic trifluoromethyl groups on the surface of the films.

9.3.3. Thermal Degradation

In the thermal degradation (TG) curves of poly(formal)s, the onset temperatures of weight loss shift to higher temperatures with increasing Bisphenol AF content.[13] The weight loss of Bisphenol A poly(formal) (**6**) occurs in a single step, whereas the weight of hexafluoroisopropylidene-unit-containing poly(formal)s decreases in two stages and the inflection at about 500°C becomes more definite with increasing Bisphenol AF content. The typical TG–DTA (differential thermal
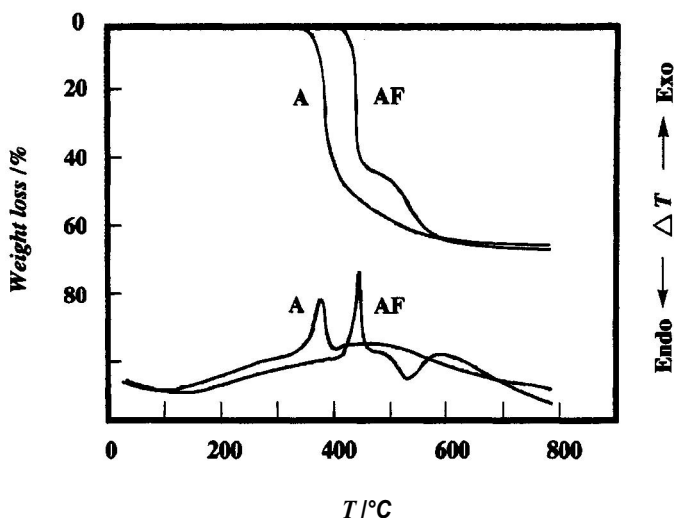

Figure 9.1. TG–DTA curves for Bisphenol A-derived poly(formal) (A) and Bisphenol AF-derived poly(formal) (AF).

analysis) curves are shown in Figure 9.1 for Bisphenol A poly(formal) **(6)** and Bisphenol AF poly(formal) **(7).** The first stage of the degradation is exothermic and the second one is endothermic in the DTA curve of Bisphenol AF poly(-formal) **(7).**

The FTIR spectra of the gas mixture evolved in thermal decomposition of Bisphenol AF poly(formal) **(7)** at various temperatures suggest the existence of benzene rings, C—O—C bonds, and C=C bonds. In a pyrogram of pyrolysis gas chromatography (Py-GC) of Bisphenol A **(3),** α-methylstyrene, phenol, *p*-cresol, 4-hydroxy-α-methylstyrene, and isopropyl phenol are observed as major peak products. The cleavage reactions shown in Scheme **(5)** is suggested for the formation of phenol and 4-hydroxy-a-methylstyrene from Bisphenol A **(3).**
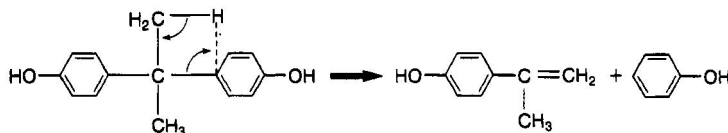
Scheme 5

In a pyrogram of Bisphenol A poly(formal) **(6),** the peak products are identified as α-methylstyrene, phenol, 4-hydroxy-α-methylstyrene, and isopropyl phenol by Py-GC/MS. These products are identical with the degradation products from Bisphenol A. In addition to the decomposition products of Bisphenol A, 4-isopropenyl anisole is also identified as a product. The pyrograms of Bisphenol AF poly(formal) **(7)** contain only two major species, pentafluoroisopropenyl benzene (product 1′) and pentafluoroisopropenyl anisole (product 2′). They correspond to α-methylstyrene, 4-hydroxy-α-methylstyrene from Bisphenol A poly(formal) **(6)** and are produced by the cleavage of phenylene–oxy bonds and oxy–methylene bonds according to (Scheme 6).
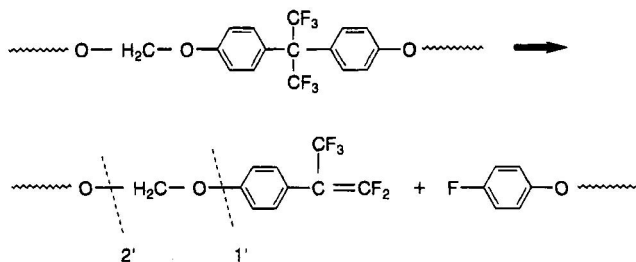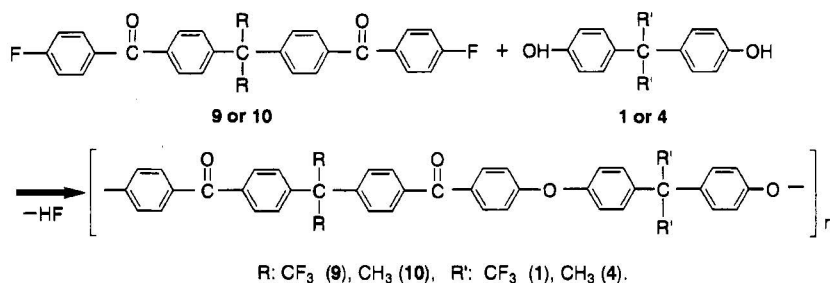

Scheme 6

The bond dissociation energy of phenylene–oxy bonds is not very different from that of oxy–methylenebonds. Accordingly, the two-step decrease in weight of hexafluoroisopropylidene-unit-containing poly(formal)s, especially Bisphenol AF poly(formal) **(7),** is not brought about by a different reaction mechanism from

that of Bisphenol A poly(formal) (**6**), but results rather from the difference in vapor pressures, (i.e., the different rates of vaporization) between product 1′ and product 2′ themselves or their polymerized products. Specifically, product 2′ is produced by Scheme (5) and the cleavage of oxy–methylene bonds, and then product 1′ is produced by the secondary degradation of product 2′. The more volatile 1′ is evaporated in the first stage and then the less volatile 2′ in the second stage, which is why the weight loss of hexafluoroisopropylidene-unit-containing poly(formal)s occurs in two steps in TG curves.

9.4. POLY(KETONE)S

9.4.1. Synthesis

Hexafluoroisopropylidene-unit-containing aromatic poly(ether ketone)s were first synthesized from an alkaline metal salt of Bisphenol AF (**1**) and 4,4′-difluoro-benzophenone.[14] Cassidy and co-workers prepared hexafluoroisopropylidene-unit-containing poly(ether ketone)s by condensing 2,2-bis[4-(4-fluorobenzoyl)-phenyl]-l,l,1,3,3,3-hexafluoropropane (**9**) and 2,2-bis[4-(4-fluorobenzoyl)-phenyl]propane (**10**) with Bisphenol AF (**1**) or Bisphenol A (**4**) (Scheme 7).[15] The reactions are nucleophilic aromatic displacements and were conducted in DMAc at 155– 160°C with an excess of anhydrous potassium carbonate. After 3 to 6 h of reaction, high-molecular-weight poly(ketone)s are obtained in high yields.


R: CF₃ (9), CH₃ (10), R': CF₃ (1), CH₃ (4).

Scheme 7

A powerful and efficient method for the preparation of poly(ketone)s is the direct polycondensation of dicarboxylic acids with aromatic compounds or of aromatic carboxylic acids using phosphorus pentoxide/methanesulfonic acid (PPMA)[16] or polyphosphoric acid (PPA)[17] as the condensing agent and solvent. By applying both of these reagents to the synthesis of hexafluoroisopropylidene-unit-containing aromatic poly(ketone)s, various types of poly(ketone)s such as poly(ether ketone) (**11**), poly(ketone) (**12**), poly(sulfide ketone) (**13**), and poly-

(sulfone ketone) **(14)** have been prepared by the reaction of 2,2-bis(4-carbox-yphenyl)-l,1,1,3,3,3-hexafluoropropane **(15)** with diphenyl compounds such as diphenyl ether, diphenyl ketone, diphenyl sulfide, and diphenyl sulfone.[18] The structures of the resulting polymers are confirmed by ^{1}H-NMR and IR.

The reaction of **15** with diphenyl ether and diphenyl sulfide yields poly(ether ketone) **(11)** and poly(sulfide ketone) **(13)** with exclusively *para*-substituted benzene rings according to Scheme 8.

X: O **(11)**, S **(13)**.
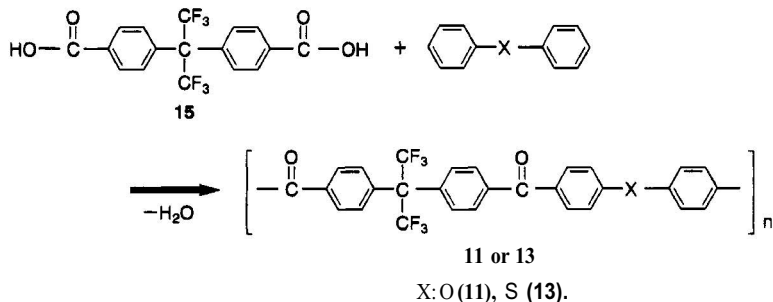
Scheme 8

Poly(ketone) **(12)** and poly(sulfone ketone) **(14)** are produced according to Scheme (9). They contain significant numbers of phenylene units substituted in *p*- and *o*-positions in addition to the *m*-phenylene units.


X: CO **(12)**, SO$_2$ **(14)**.
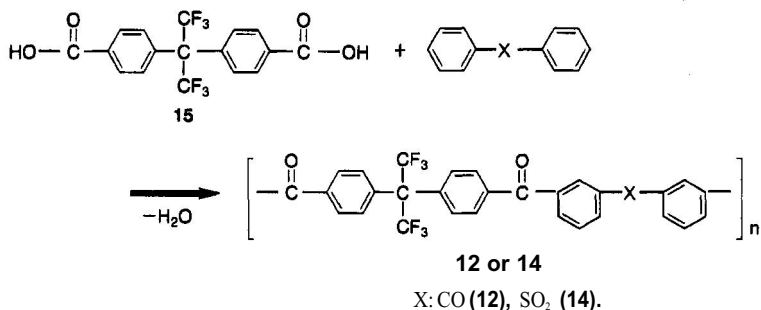
Scheme 9

Reaction temperatures below 100°C and high monomer concentrations are essential for preparing polymers with higher molecular weights in high yields. All of the polymerizations proceed in homogeneous solutions. However, higher monomer concentration, i.e., one molar monomer solution in PPMA causes precipitation of the polymers during the reaction and restricts the molecular weight of the polymers to a low value.

The molecular weights of poly(ketone)s obtained from diphenyl ketone and diphenyl sulfone are lower than those from diphenyl ether and diphenyl sulfide. The former monomers possess highly electron-withdrawing carbonyl or sulfone groups, which lower the electron density of the rings.

Hexafluoroisopropylidene-unit-containing copoly(ether ketone)s and copoly-(sulfide ketone)s are also synthesized by reacting mixtures of 2,2-bis(4-carboxy-phenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** and 2,2-bis(4-carboxyphenyl)-propane **(16)** with diphenyl ether or diphenyl sulfide in PPMA, respectively (Scheme 10).[18]

x: O or S
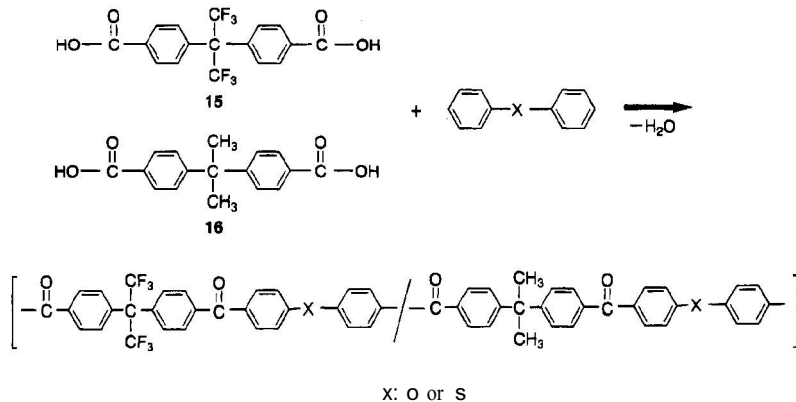
Scheme 10

Irrespective of the feed ratio of **15** and **16,** the reaction proceeds homogeneously, and quantitative yields are attained with reduced viscosities between 0.13 and 0.37 dl/g.

9.4.2. Properties

Four poly(ether ketone)s obtained from 2,2-bis[4-(4-fluorobenzoyl)-phenyl]-1,l,1,3,3,3-hexafluoropropane **(9)** or 2,2-bis[4-(4-fluorobenzoyl)-phenyl]propane **(10)** with Bisphenol AF **(1)** or Bisphenol A **(4)** are all soluble in chloroform, benzene, THF, and aprotic polar solvents such as DMF, DMAc, and NMP.[15] Poly(ether ketone) from **9** and **1,** which has the highest fluorine content, dissolves easily in ethyl acetate.

The T_g of the poly(ether ketone) from **9** and **1** is 180°C.[15] This is the highest among the four poly(ether ketone)s and higher by 30°C than that of PEEK. The T_g of poly(ether ketone) from **10** and **4** having no fluorine atom shows the lowest T_g of 169°C because of the smaller steric hindrance of methyl groups to the free rotation of the polymer backbone compared to more bulky trifluoromethyl groups. Thermal stability of these poly(ether ketone)s is high. The DT[10] of the poly(ether ketone) from **9** and **1** is 485°C in air and 536°C in nitrogen, respectively. A membrane from poly(ether ketone) from **9** and **1** shows high selectivity ratios for H_2/CH_4 and CO_2/CH_4.

Poly(ketone)s obtained from 2,2-bis(4-carboxyphenyl)-1 1,1,3,3,3-hexa-fluoro-propane **15** with diphenyl compounds dissolve readily in aprotic polar

Table 9.8. Thermal Properties of Poly(Ketone)s
Having Hexafluoroisopropylidene Units[18]

Polymer	T_g (°C)	T_m (°C)	DT$_5$ (°C)	RW (%)
11	171	—	> 500	98
12	158	202	> 500	96
13	134	—	338	78
14	142	—	338	74

solvents such as DMF, DMAc, DMSO, and NMP and even in m-cresol, sulfolane, trichloroethane, and THF.[18]

Crystallinity of these hexafluoroisopropylidene-unit-containing poly(ketone)s is low except for poly(sulfide ketone) **(13).** The water contact angle for the fluorine-containing poly(ketone) films is high, being 98° for poly(ether ketone) **(11),** from 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** and 96° for poly(sulfide ketone) **(13)** from **15,** whereas it is 78° for poly(ether ketone) from 2,2-bis(4-carboxy-phenyl)propane **(16)** and 74° for the poly(sulfide ketone) from **16.** This result indicates that the substitution of isopropylidene units of poly-(ketone)s with hexafluoroisopropylidene units has a remarkable effect on the surface properties of poly(ketone) films.

The T_g of hexafluoroisopropylidene-unit-containing poly(ether ketone) **(11)** is 171°C, which is higher than that of the hexafluoroisopropylidene-unit-containing poly(sulfide ketone) **(13)** by 13°C (Table 9.8).18 The T_g for the former **(11)** is remarkably higher than those of 144 and 155°C for PEEK and PEK, respectively. The T_g values of poly(ether ketone) and poly(sulfide ketone) having no fluorine atoms from **16** and dipheny; ether or diphenyl sulfide are 134 and 142°C. Hexafluoroisopropylidene-unit-containing poly(sulfide ketone) **(13)** shows a melting point of 202°C, whereas other hexafluoroisopropylidene unit-containing poly(ketone)s are amorphous.

Thermooxidative stability of the fluorine-containing poly(ether ketone) **(11)** and poly(sulfide ketone) **(13)** from **15** is very high. The 5% weight-loss temperatures (DT5) are 391 and 436°C for poly(ether ketone) and poly(sulfide ketone) analogues having no fluorine atoms, whereas those of poly(ether ketone) **(11)** and poly(sulfide ketone) **(13)** are higher than 500°C.
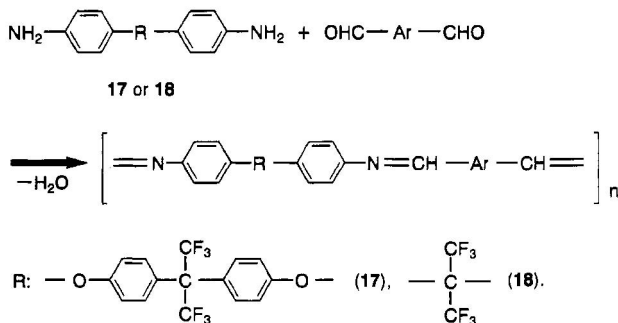
9.5. POLY(AZOMETHINE)S

9.5.1. Synthesis

Many approaches have been attempted to obtain soluble or fusible high-molecular-weight poly(azomethine)s, including the introduction of flexible

bonds, spacers, or pendant bulky groups to the polymer backbone and ring substitutions.

Novel fluorine-containing aromatic poly(azomethine)s are prepared by the reaction of hexafluoroisopropylidene-unit-containing aromatic diamines, 2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (**17**) and 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane (**18**) with terephthalaldehyde (**19**) or isophthalaldehyde (**20**)[20] (Scheme 11).
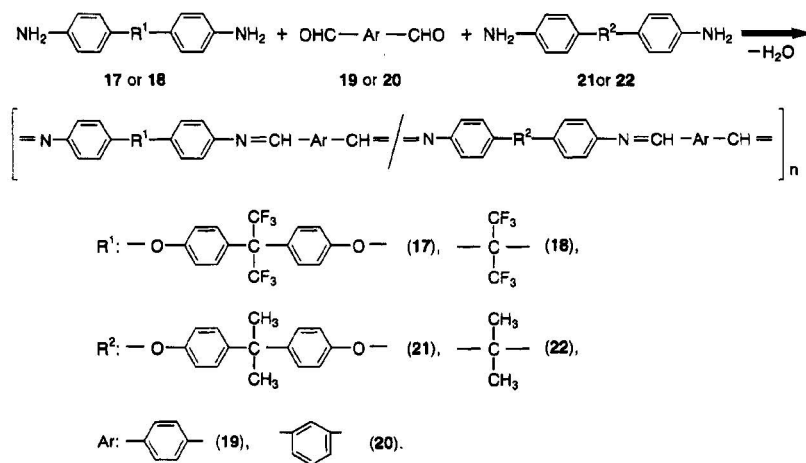

Scheme 11

Room-temperature solution polycondensation is used for the preparation of hexafluoroisopropylidene-unit-containing poly(azomethine)s. At the end of the reaction, the water liberated by the reaction is thoroughly taken off as an azeotrope by vacuum distillation to allow the reaction to go to completion. Among DMF, DMSO, HMPA, NMP, and *m*-cresol used as reaction solvents, *m*-cresol yields a polymer with higher reduced viscosity in higher yield. The reaction proceeds rapidly and is essentially completed in 30 min.

Hexafluoroisopropylidene-unit-containing copoly(azomethine)s are also prepared under similar reaction conditions using an equimolar mixture of 2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (**17**) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**21**) or of 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane (**18**) and 2,2-bis(4-aminophenyl)propane (**22**) as the diamine components with terephthalaldehyde (**19**) or isophthalaldehyde (**20**) (Scheme 12).[20]

9.5.2. Properties

Wholly aromatic poly(azomethine)s possess remarkable thermal stability, and high strength and modulus. However, owing to their limited solubility and infusibility, it is difficult to obtain poly(azomethine)s having sufficiently high molecular weight and useful processability.

The incorporation of fluorine atoms improves the solubility of aromatic condensation polymers without causing them to lose their high thermal stability and modifies the processability. Hexafluoroisopropylidene-unit-containing poly-(azomethine)s and copoly(azomethine)s are readily soluble in highly polar solvents such as DMAc, HMPA, and NMP, and they also dissolve completely in dichloromethane, chloroform, and THF, whereas poly(azomethine)s derived from **21** and **22** and having no fluorine atom are insoluble in these solvents.[20] Accordingly, the solubility of aromatic poly(azomethine)s is remarkably improved by substituting isopropylidene units with fluorine atoms.

Scheme 12

The cast films of poly(azomethine)s are transparent but pale to deep yellow in color. The water contact angles of fluorine-containing poly(azomethine)s films from diamine (**17**) are 80° for terephthalaldehye (**19**) and 75° for isophthalalde-hyde (**20**) as dialdehyde component (Table 9.9).[20] These low values of water contact angles are attributed to the lower fluorine content in these polymers.

None of the poly(azomethine)s show glass transition, and they are amorphous irrespective of the presence or absence of fluorine atoms[20] All the poly(azomethine)s are thermooxidatively stable at temperatures as high as 400°C. Hexafluoroisopropylidene-unit-containing poly(azomethine)s are more stable to thermooxidation than those having no fluorine atom (Table 9.9). This is expected because the methyl group is more susceptible to oxidation than aromatic rings.

Table 9.9. Preparation and Properties of Poly(Azomethine)s Having Hexafluoroisopropylidene Units[20]

Polymer		Contact angle[a] (degree)	DT_5 (°C)
Diamine	Dialdehyde		
17	19	80	467
	20	75	490
18	19	—	443
	20	—	486
11	19	—	452
	20	71	479
12	19	—	420
	20	—	475

[a]Water contact angle at 20°C in air.

9.6. POLY(AZOLE)S

9.6.1. Synthesis

Several routes have been reported for the synthesis of aromatic poly(azole)s such as poly(benzimidazole), poly(benzoaxazole), and poly(benzthiazole): melt polycondensation of dicarboxylic acid diphenyl esters with tetramines[21] and high-temperature solution polycondensation of dicarboxylic acids or their derivatives with tetramine hydrochlorides in PPA.[22] PPA acts as condensing agent and solvent. Ueda *et al.*[23] developed a modified method for the synthesis of polyazoles with the use of PPMA.

Fluorine-containing aromatic poly(benzimidazole)s are synthesized by direct polycondensation of 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** with 3,3′-diaminobenzidine tetrahydrochloride **(23)** (Scheme 13) and 1,2,4,5-benzenetetramine tetrahydrochloride **(24)** (Scheme 14) in PMMA or PPA.[24]
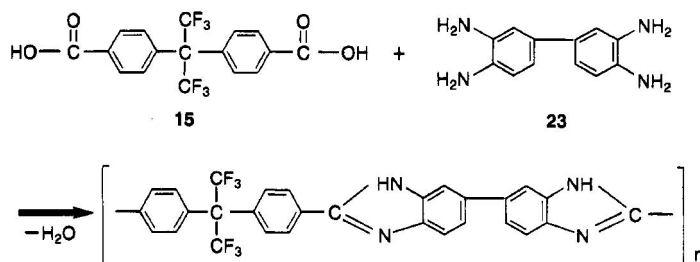
Scheme 13
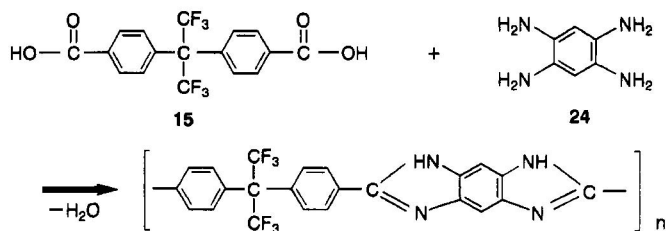
Scheme 14

The effects of various reaction conditions are examined in detail, in which 1 mmol of tetramine **(23)** or **(24)** is reacted with 1 mmol of dicarboxylic acid **(15)**. As for the amount of solvent, 5 ml of PPMA is appropriate for the 1-mmol scale reaction. A higher concentration makes it difficult for the reaction to proceed homogeneously, whereas a lower concentration reduces the rate of reaction. The reduced viscosity markedly increases with increasing temperature, and the poly-condensation of **15** and benzidine **(23)** at 140°C results in a sufficiently high reduced viscosity of 0.90 dl/g in 24 h. The reaction of 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** with tetramines occurs slowly, requiring more than 24 h for completion, because **(15)** has the highly negative hexafluoroisopro-pylidene unit.

The reduced viscosity of poly(benzimidazole) from **15** and tetramine **(24)** is not high enough under the reaction conditions described above in PPMA. The reaction at 200°C for 24 h in PPMA affords only a low-molecular-weight polymer in a low yield owing to low solubility in PPMA and sublimation of dicarboxylic acid (15). However, an improved reduced viscosity of 0.59 dl/g is attained by a two-step method, first at 140°C for 24 h and then at 200°C for 24 h.

High-molecular-weight fluorine-containing aromatic poly(benzoxazole)s have not been obtained either by the direct solution polycondensation in PPA at 200°C or by the low-temperature solution polycondensation in DMAc at 0 to 5°C from 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and aromatic diacid derivatives because the fluorine-containing monomer has low nucleophilicity owing to the presence of the electron-withdrawing hexafluoroiso-propylidene unit.

Maruyama et al.[25] have obtained high-molecular-weight poly(benzoxazole)s by the low-temperature solution polycondensation of $N,N´,O,O´$-tetrais(trimethyl-silyl)-substituted 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoro-propane **(25)** with aromatic diacids and subsequent thermal cyclodehydration of the resulting poly(o-hydroxy amide)s *in vacuo.* In this method, aromatic diamines with low nucleophilicity are activated more positively through the conversion to the *N*-silylated diamines, and the nucleophilicity of the fluorine-containing bis(o-aminophenol) can be improved by silylation.

The low-temperature solution polycondensation of **25** with dichloride **(26)** of 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** is carried out in

DMAc at 0 to 5°C for 8 h and fluorine-containing poly(*o*-hydroxy amides) **(27)** having an inherent viscosity of 0.40 dl/g is obtained (Scheme 15).[25]
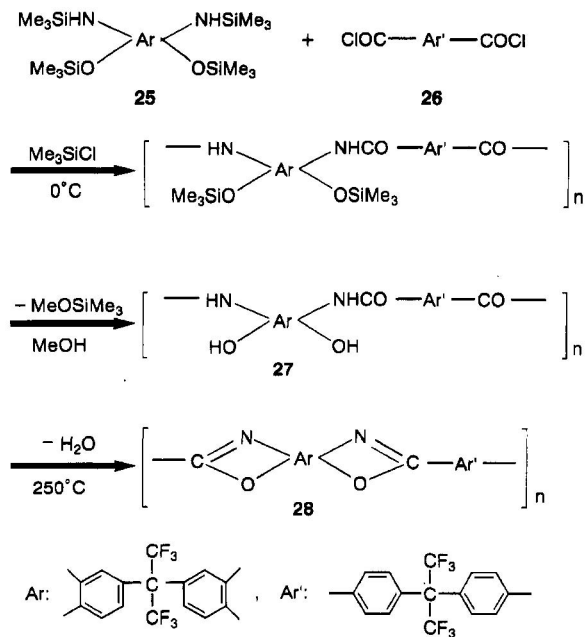
Scheme 15

In the second stage, the poly(*o*-hydroxy amides) **(27)** are subjected to thermal cyclodehydration to convert to poly(benzoxazole) **(28).** The conversion requires 15 to 20 h at 250°C *in vacuo* for its completion. The resulting poly(benzoxazole) **(28)** has an inherent viscosity of 0.49 dl/g.

Fluorine-containing aromatic poly(benzothiazole)s are synthesized by direct polycondensation of 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane **(15)** with 2,5-diamino-1,4,-benzenedithiol dihydrochloride **(29)** using PPMA or PPA as both condensing agent and solvent (Scheme 16).[26]
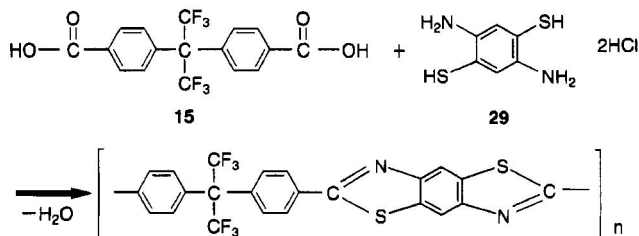
Scheme 16

The direct polycondensation of **15** with **29** in PPMA at 140°C for 24 h does not yield polymers having high enough reduced viscosity to produce a tough film. The prolonged reaction is not successful. The low reactivity of **15** is associated with a strongly electron-withdrawing hexafluoroisopropylidene group at the *para* position to the carboxyl groups. The conventional PPA method conducted at 200°C affords only a low-molecular-weight polymer in low yield owing to the low solubility of **15** in PPA and its sublimation. High-molecular-weight polymer is successfully obtained by a two-step reaction, first at 140°C for 48 h and then at 200°C for 24 h.

High-molecular-weight aromatic poly(benzothiazole)s can be obtained from dichloride **(26)** of **15** and **29** in PPA under similar reaction conditions (Scheme 17).
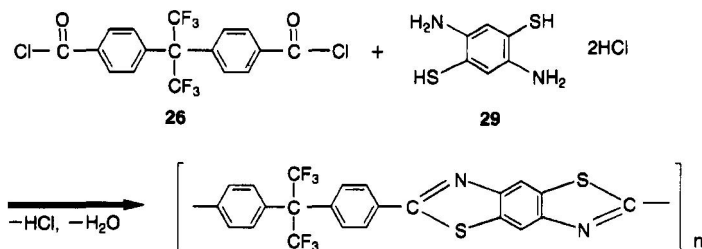
Scheme 17

9.6.2. Properties

Poly(benzimidazole)s possess excellent thermal stability, flame resistance, and outstanding chemical resistance. The solubility of hexafluoroisopropylidene-unit-containing poly(benzimidazole)s is remarkably improved.[24] They are readily soluble in strong acids such as formic acid, concentrated sulfuric acid, and methanesulfonic acid and in aprotic polar solvents such as DMAc and NMP. The polymer from tetramine **(23)** is soluble even in *m*-cresol and pyridine.

These poly(benzimidizole)s are amorphous.[24] The T_g of the polymer from tetramine **(23)** is 330°C, and no glass transition is observed for the polymer from tetramine **(24).** The former T_g value is higher (280 to 325°C) than those of the hexafluoroisopropylidene-unit containing poly(benzoxazole)s.[25]

The thermal stability of poly(benzimidazole) is further improved by the introduction of hexafluoroisopropylidene units in the main chain. The DT_{10} is 520°C in air and greater than 520°C in nitrogen for the polymer from

tetramine **(23)** and 506°C in air and greater than 520°C in nitrogen for that from tetramine **(24).**

The increased solubility and amorphous nature of this polymer is ascribed to reduced intermolecular forces between the polymer chains owing to the introduction of fluorine atoms and to looser packing owing to the highly distorted diphenylhexafluoroisopropylidene units in the polymer backbone.

Aromatic poly(benzoxazole)s exhibit excellent thermal stability. Rigid-rod poly(benzoxazole)s are fabricated into high-strength and high-modulus fibers. Fluorine-containing aromatic poly(benzoxarole)s are expected to have unique properties.

The precursor of poly(penzoxazole) **(28),** poly(o-hydroxy amide) **(27)** is amorphous and readily soluble in DMF, NMP, DMSO, pyridine, THF, and acetone.[25] Transparent, flexible, and tough film of **27** can be obtained by casting. However, fluorine-containing poly(benzoxazole) **(28)** from **25** dissolves only in concentrated sulfuric acid and o-chlorophenol.

The poly(benzoxazole) **(28)** has a T_g of   295°C. The DT_{10} is 525°C in air and 530°C in nitrogen, respectively.[25]

Aromatic poly(benzothiazole)s are thermally and thermooxidatively stable and have outstanding chemical resistance and third-order nonlinear optical susceptibility. Aromatic poly(benzothiazole)s can be spun into highly-oriented ultrahigh strength and ultrahigh modulus fibers. However, this type of polymer is insoluble in most organic solvents. Therefore, hexafluoroisopropylidene units are introduced in the polymer backbone to obtain soluble or processable aromatic poly(benzothiazole)s.

The aromatic poly(benzothiazole) from **15** and **29** is almost amorphous and easily soluble in strong acids such as concentrated sulfuric acid and methanesulfonic acid.[26] It also dissolves in organic solvents such as HMPA and o-chlorophenol. The increased solubility and amorphous nature of this polymer is also ascribed to reduced intermolecular forces and to looser packing owing to the presence of highly distorted diphenylhexafluoroisopropylidene units in the polymer backbone.

Transparent, flexible, and tough films with deep orange color are cast from HMPA solution of poly(benzothiazole) from **15** and **29.**[26] The tensile strength of 69 Mpa and the tensile modulus of 2.7 GPa are obtained for aromatic poly(benzoxazole) **(28)** from **15** and **29.** These values are higher than those of hexafluoroisopropylidene-unit-containing poly(benzimidazole).

The T_g of hexafluoroisopropylidene-unit-containing poly(benzthiazole) is 327°C, which is almost the same as that of hexafluoroisopropylidene-unit-containing poly(benzimidazole). The hexafluoroisopropylidene-unit-containing poly(benzthiazole) is stable up to 470°C in both air and nitrogen. The thermal stability of the hexafluoroisopropylidene-unit-containing poly(benzimidazole) is almost comparable to that of the hexafluoroisopropylidene-unit-containing poly(benzimidazole). The DT_{10} is 527°C in air and 537°C in nitrogen.

9.7. POLY(SILOXANE)

9.7.1. Synthesis

Novel poly(aryloxydiphenylsilane) is prepared from Bisphenol AF (2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane) **(1)** and dianilinodiphenylsilane **(30)** by melt polycondensation at elevated temperatures under reduced pressure of 1 to 2 Torr (Scheme 18).[27] The molecular weight of the poly-(aryloxydiphenylsilane) derived from anilinosilane and bisphenols have been reported to be highly dependent on the reaction temperature in the melt polycondensation.[28]
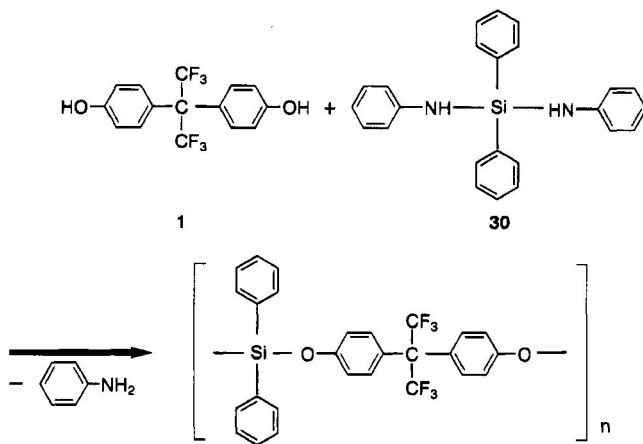
Scheme 18

The most suitable reaction temperature for obtaining a high-molecular-weight polymer is 320°C, and the chloroform-soluble polymer having the reduced visibility of 0.31 dl/g is obtained in a reaction time of 2 h.[27] At higher reaction temperatures, the insoluble fraction occurs owing to cross-linking of polymers. The reduced viscosity of Bisphenol-AF-derived poly(aryloxydiphenylsilane) is not high, which is attributed to the decrease in nucleophilicity of the bisphenol induced by strong electron attraction of fluorine atoms.

9.7.2. Properties

Poly(organosiloxane)s have a number of outstanding properties such as thermal and oxidative stability, water and chemical resistance, electric insulating capacity, selective permeability to gases, and biocompatibility.

Usually, silicon polymers have extremely low T_g's owing to the highly flexible Si—O linkages in the main chain. Their low T_g's are very advantageous for low-temperature applications, whereas some other applications are limited. One approach to raise the T_g of silicon polymers is the introduction of aromatic rings into the polymer backbone.

X-ray diffraction measurements have shown that Bisphenol-AF-derived poly(aryloxydiphenylsilane) is amorphous.[28] The T_g value of 106°C is higher than that of the poly(aryloxydiphenylsilane)s derived from dianilinodiphenylsilane and bisphenols such as 4,4′-biphenol, 2,7-dihydroxynaphthalene, and hydroquinone.[28] The aromatic units in poly(aryloxy-diphenylsilane(s) have a remarkable effect on the T_g. The thermal stability of this polymer is somewhat lower than those of poly(aryloxydiphenylsilane)s derived from dianilinodiphenylsilane and bisphenols such as 4,4′-biphenol, 2,7-dihydroxynaphthalene, and hydroquinone. The DT10 is 362°C and the residual weight at 500°C in air is 54%.

Bisphenol-AF-derived poly(aryloxydiphenylsilane) dissolves easily in a wide variety of organic solvents, including chlorinated and aromatic hydrocarbons, cyclic ethers, and aprotic polar solvents.

The UV transmission of Bisphenol-AF-derived poly(aryloxydiphenylsilane) shows a very sharp cut-off at about 285 nm (Figure 9.2).
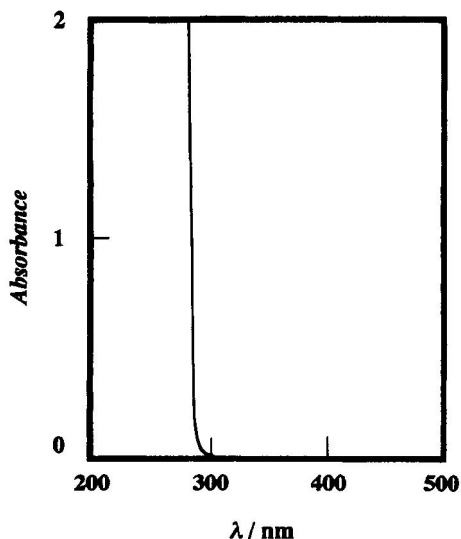

Figure 9.2. UV transmission of poly(aryloxydiphenylsilane) film obtained from Bisphenol AF and dianilinodiphenylsilane.

9.8. CONCLUSIONS

The solubility, water and oil repellency, thermal and thermooxidative stability, and T_g are enhanced and crystallinity and water absorption are decreased by introducing hexafluoroisopropylidene units, rather than units of isopropylidene, into polymer backbone of aromatic condensation polymers.

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