Synthesis and Characterization of Fluorinated Poly(imide–amide–sulfone)s

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SYNOPSIS

A series of new, fluorinated poly(imide–amide–sulfone)s has been synthesized by solution polycondensation of aromatic diamines containing sulfone groups with diacid chlorides incorporating both imide and hexafluoroisopropylidene units. These polymers are soluble in polar amidic solvents, and their solutions can be cast into colorless, thin, flexible films having good electrical insulating properties and high thermal stability. The dielectric constant value is 3.49–3.68. The decomposition temperature in air is 464–479°C, and the glass transition temperature is in the range 279–359°C. All these characteristics have been discussed and compared with those of related fluorinated poly(imide–amide)s which do not contain sulfone groups and with other imide polymers without hexafluoroisopropylidene units. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The necessity of using heat-resistant materials in the aerospace and microelectronics industries has led to an expanding development of research on different heterocyclic polymers with targeted applications as dielectric films, interlayer dielectrics, or passivation coatings in integrated circuits. For this purpose, it is desirable to use heterocyclic polymers which are fully cyclized and soluble for spin-coating and casting processes. Polyimides are generally the polymers of choice for these applications due to their unique combination of chemical, physical, and mechanical properties.[1] However, fully aromatic polyimides are completely insoluble and infusible; their glass transition temperatures, being very high, practically in the same range with their decomposition, make their processing possible only from poly(amic acid) intermediates. The widely utilized two-stage process for the manufacture of polyimides from poly(amic acid)s still has some disadvantages connected with the limited storage stability of the intermediate poly(amic acid)s and with the evolution of low molecular weight volatile products during the polyheterocyclization.

Many attempts have been made to improve the processing properties of aromatic polyimides, particularly their solubility and fusibility, by introducing amide, ester, ether, or other flexibilizing groups into the main chain.[2] Considerable attention has been devoted lately to the synthesis of fluorine-containing polyimides, particularly to those with hexafluoroisopropylidene (6F) groups. Frequently, the incorporation of 6F groups into a polymer backbone will improve the solubility and other properties such as flame resistance, thermal stability, oxidation resistance, and environmental stability, while there is often a decrease in color, crystallinity, dielectric constant, and moisture absorption.[3]

In our continuing effort to develop easily processable high-performance polymers which have both high thermal stability and a low dielectric constant, we prepared a series of fluorinated poly(imide–amide–sulfone)s and characterized their thermal and electrical properties. The incorporation of sulfone groups into the macromolecular chain often generates interesting properties such as increased glass transition and higher decomposition temperatures and can also lead to liquid crystallinity, due to the strong interactions between sulfone groups.[4]
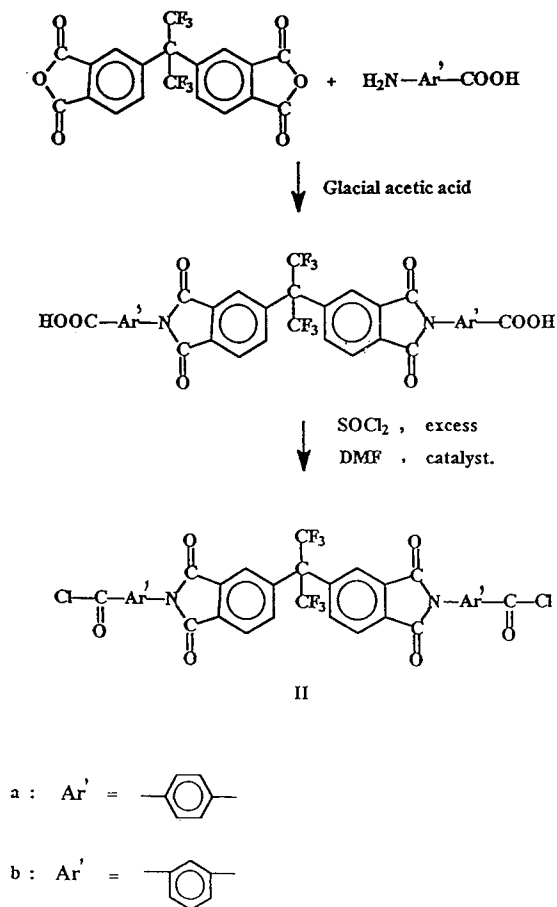
Scheme 1

The fluorinated poly(imide–amide–sulfone)s reported herein have been prepared by reaction of an aromatic diamine having sulfone groups with a diacid chloride containing preformed imide rings and hexafluoroisopropylidene groups. For comparison, related poly(imide–amide)s without sulfone groups have been prepared from 4,4'-diaminodiphenyl ether with the same diacid chlorides.

EXPERIMENTAL

Starting Materials

Aromatic diamines, **I**, such a 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-(p-aminophenoxy)diphenyl sulfone, and 4,4'-diaminodiphenyl ether were obtained from Aldrich and purified by recrystallization from ethanol. Hexafluoroisopropylidene diphthalic anhydride (6FDA) was a gift from Hoechst Celanese and it was used without purification. The p- and m-aminobenzoic acid, glacial acetic acid, thionyl chloride, benzene, n-hexane,

pyridine (Py), and N-methylpyrrolidinone (NMP) were all obtained from Aldrich. Thionyl chloride was distilled before use. N-Methylpyrrolidinone was distilled over phosphorous pentoxide under reduced pressure.

## Synthesis of the Diacid Chlorides

Diacid chlorides containing imide and hexafluoroisopropylidene groups, **II**, were synthesized in two steps: First, the reaction of 1 mol hexafluoroisopropylidene diphthalic anhydride with 2 mol p- or m-aminobenzoic acid was performed in refluxing glacial acetic acid instead of using polar amidic solvents as previously reported.[5] Thus, the intermediate fluorinated diimide–diacids separated from the reaction mixture as white crystalline products. After washing with ethanol and drying, they were treated with excess thionyl chloride at reflux, using dimethylformamide as a catalyst. Diacid chloride **IIa** separated during the reaction as a white crystalline compound, and it was filtered, washed with n-hexane, and dried in vacuo: m.p. 315–317°C. To isolate the diacid chloride **IIb**, the excess thionyl chloride was removed under vacuum and the residue was dissolved in hot benzene. Crystallization, induced by adding n-hexane, gave a white product: m.p. 214–216°C.

Synthesis of the Polymers

Low-temperature solution polycondensation of equimolar amounts of diamine, **I**, and diacid chloride, **II**, was carried out in N-methylpyrrolidinone using pyridine as the acid acceptor to give the fluorinated poly(imide–amide–sulfone)s, **III**.

Polycondensations were performed by adding the powdered diacid chloride to a solution of the diamine in NMP + Py with stirring under argon at −10°C. After addition of the diacid chloride, the concentration of the solution was 8–10% solids. A typical polymerization was carried out as follows:

To a 100 mL three-neck flask equipped with a mechanical stirrer and an argon inlet and outlet was added 1.24 g (0.005 mol) of 4,4'-diaminodiphenyl sulfone, 40 mL NMP, and 0.4 mL Py. The mixture was stirred under argon until complete dissolution, then cooled in an ice bath at −10°C, and 3.59 g (0.005 mol) diacid chloride, **IIa**, was added through a funnel, with rapid stirring. The funnel was washed with an additional 5 mL NMP. The reaction temperature was maintained below 0°C for 15 min; then, the temperature was allowed to increase to 20°C in the following 15 min, and
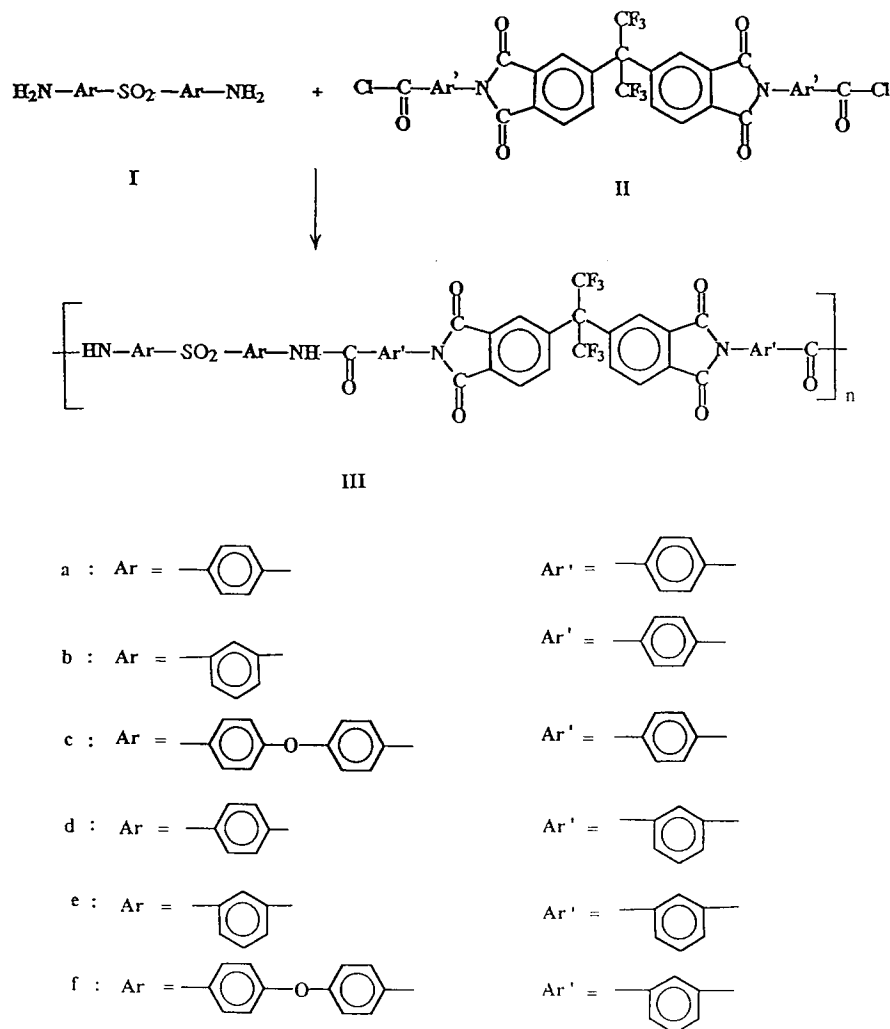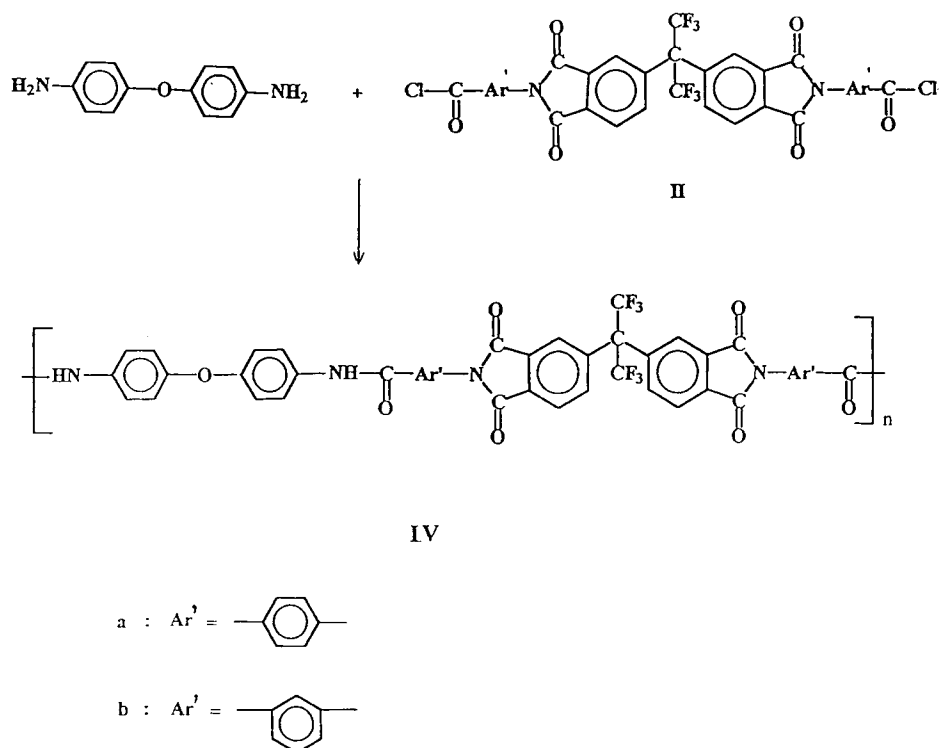
Scheme 2

the stirring was continued at this temperature for 4 h. Half of the resulting viscous polymer solution was cast onto glass plates (size 100 × 100 mm) and dried by heating at 100, 140, 180, and 210°C each for 1 h. A transparent film resulted, which was stripped off the glass plate and used for various measurements. The other half of the polymer solution was diluted with 20 mL NMP and was poured into water under rapid stirring. The precipitated fibrous product was filtered, washed twice with water and once with ethanol under stirring, and dried in a vacuum oven at 120°C for 2 h.

Measurements

The inherent viscosity of the polymers was determined at 20°C for solutions having the concentration of 0.5 g polymer/100 mL NMP, using an Ubbelohde viscometer. Infrared spectra were recorded on a Perkin–Elmer 1600 Series Fourier transform infrared (FTIR) spectrometer at 4 cm^{-1} resolution and 16 scans, using polymer films of 3–6 μm thickness. Glass transition temperatures (T_g) of the precipitated polymers, taken as the midpoint of the change in slope of the base line, were determined using differential scanning calorimetry (DSC) at a heating rate of 10°C/min, in nitrogen. Thermal stability was investigated by thermogravimetric analysis (TGA), at a heating rate of 20°C/min, in air. Both DSC and TGA were performed on a Perkin-Elmer Series 7 DSC/TGA.

Dielectric constants were determined on polymer films of 20–30 μm thickness, using the previously described fluid displacement method.[6] The capacitance of the films was measured using circular gold

Scheme 3

RESULTS AND DISCUSSION

Aromatic diamines containing sulfone groups, Ia–c, and the diamine containing only the ether group, Id, were commercially available and were purified by recrystallization. Diacid chlorides, II, were readily prepared in high yield from hexafluoroisopropylidene diphthalic anhydride and p- or m-aminobenzoic acid through reaction of the diimide–diacids intermediate with thionyl chloride in the second step (Scheme 1). The use of glacial acetic acid as a solvent in the process of the intermediate gave a purer product when compared to similar products prepared in amidic solvents[5]; therefore, the diimide–diacid intermediate was used directly in the second step to afford the desired diacid chloride.
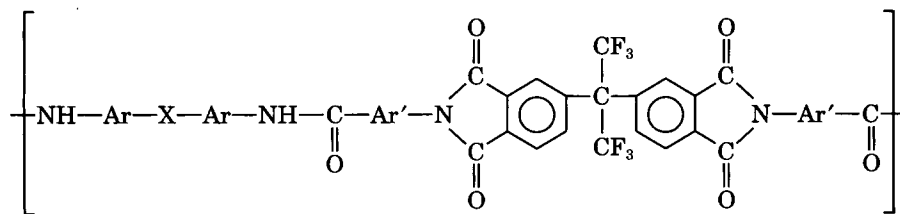
Polycondensations of equimolar amounts of diamines, I, and diacid chlorides, II, in NMP, at low temperature yielded viscous solutions of fluorinated poly(imide–amide–sulfone)s, III (Scheme 2). For comparison, related poly(imide–amide)s, IV, with-

out sulfone groups were prepared from 4,4'-diaminodiphenyl ether and the same diacid chlorides (Scheme 3).

Solutions of all the polymers were coated onto glass substrates and dried to yield transparent flexible films. Parallel workup in water of NMP solutions yielded fibrous products which were white in the case of polymers III and yellow in the case of polymers IV. The expected structures of poly(imide–amide–sulfone)s, III, and related poly(imide–amide)s, IV, were confirmed by FTIR data as follows: The strong bands appearing at 1785–1782 cm^{-1}, 1726–1724 cm^{-1}, and 721–719 cm^{-1} were assigned to the imide rings. These bands are also present in the spectra of preformed imide monomers, II. The amide groups from the polymer backbone were identified through the broad absorption at 3371–3346 cm^{-1}, characteristic for NH, and at 1683–1667 cm^{-1}, due to CO in amide groups.

All these polymers are easily soluble at room temperature in polar aprotic solvents such as N-methylpyrrolidinone, dimethylformamide, and dimethylacetamide, up to a concentration of 50% wt/vol. The improved solubility of these polymers as compared to that of related poly(imide–amide)s and other imide copolymers[7] can be explained by the

Table I Polymer Properties—General Formula:

$$\left[-NH-Ar-X-Ar-NH-\overset{O}{\underset{O}{C}}-Ar'-N\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{}}\right.\!\!\!\!\!\!\!\!\left.\overset{CF_3}{\underset{CF_3}{C}}\!\!\!\!\!\!\!\!\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{}}N-Ar'-\overset{O}{\underset{O}{C}}-\right]_n$$

Polymer	Ar	X	Ar'	η_{inh}	IDT[a] (°C)	Weight Loss at 515°C (%)	T_g (°C)	Dielectric Constant
IIIa	*p*-phenylene	SO₂	*p*-phenylene	0.59	468	13.5	359	3.55
IIIb	*m*-phenylene	SO₂	*p*-phenylene	0.65	479	9.5	295	3.63
IIIc	*p*-C₆H₄–O–C₆H₄-*p*	SO₂	*p*-phenylene	1.24	477	15.3	311	3.54
IIId	*p*-phenylene	SO₂	*m*-phenylene	0.51	472	11.5	316	3.68
IIIe	*m*-phenylene	SO₂	*m*-phenylene	0.63	473	13.1	283	3.54
IIIf	*p*-C₆H₄–O–C₆H₄-*p*	SO₂	*m*-phenylene	0.83	468	15.1	279	3.49
IVa	*p*-phenylene	O	*p*-phenylene	1.12	468	14.9	329	3.62
IVb	*p*-phenylene	O	*m*-phenylene	0.93	464	14.1	286	3.69

[a] Initial decomposition temperature.

presence of the hexafluoroisopropylidene units. Due to these groups, the packing of macromolecular chains in tight structures through hydrogen bonding between amide groups is probably disturbed and, consequently, the solvent molecules can penetrate easily to solubilize the chains.

Inherent viscosities are 0.51–1.24 dL/g (Table I). The polymers **IIIa, b,** and **c** and **IVa** obtained from diacid chloride, **IIa,** have slightly higher viscosities than do the corresponding products **IIId, e,** and **f,** and **IVb** prepared from diacid chloride, **IIb,** which could be explained by the higher reactivity of the diacid chloride, **IIa,** containing *para*-substituted phenylene rings. Similar behavior of such diacid chlorides was previously noticed when reacting with heterocyclic diamines.[5]

All the new polymers possess outstanding film-forming properties. Transparent flexible films have been obtained by casting polymer solutions from NMP onto glass plates, followed by gradually heating up to 210°C to remove the solvent. Even the polymers **IIIa** and **IIId** which have the lowest viscosities gave quite flexible films. This can be explained by the flexibilizing effect of hexafluoroisopropylidene bridges present in the main chain. Films prepared from polymer **III** are colorless, while those

made from polymers **IV**, which do not contain any sulfone groups, are yellow.

Thermogravimetric analysis shows that the polymers are highly thermostable, with decomposition beginning at 464–479°C (Table I). At 515°C, the total weight loss is 9.5–15.3%. There is no significant difference in thermal stability between polymers **III** containing sulfone groups and polymers **IV** containing only ether groups. Glass transition temperatures (T_g) of the new polymers are in the range 279–359°C (Table I). Polymers **IIIa, b,** and **c** and **IVa**, which contain a larger amount of *para*-substituted phenylene rings, have higher T_g, 359, 295, 311, and 329°C respectively, than do the analogous polymers **IIId, e,** and **f** and **IVb**, which contain a larger amount of *meta*-substituted phenylene rings and whose T_g's are 316, 283, 279, and 286°C, respectively. Thus, the expected effect of *meta*-structures on the decrease of T_g is very clearly observed. Also, it is interesting to notice that polymers **IIIa** and **IIId**, prepared from 4,4'-diaminodiphenyl sulfone, whose T_g's are 359 and 316°C, respectively, are ranged above the related polymers **IVa** and **IVb**, made from 4,4'-diaminodiphenyl ether, whose T_g's are 329 and 286°C, respectively. The increased T_g of polymers **IIIa** and **IIId** could be explained by the strong interactions between sulfone groups in the main chain. Finally, among all these compounds, polymer **IIIf** has the lowest T_g, 279°C, which is due to the combined effects of *meta*-structures with the highest amount of flexible bridges, $-SO_2-$ and $-O-$, per elemental unit of the macromolecule. The large window between T_g and the decomposition temperature makes these polymers attractive for practical processing.

The electrical-insulating property of these polymers has been evaluated on the basis of dielectric constant measurements at 0% relative humidity. The dielectric constants of polymer films are in the range 3.49–3.68 (Table I) and are very close to the dielectric constant (3.5) of the polyimide "H film" prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether, which is one of the most common polyimides used as a dielectric in microelectronic applications.[8] This shows that the introduction of hexafluoroisopropylidene units into the main chain does not affect significantly the electrical properties, probably because both amide and sulfone groups, which are very polar, are also present in the macromolecule.

CONCLUSIONS

A series of poly(imide–amide–sulfone)s containing hexafluoroisopropylidene bridges in the main chain have been prepared and compared with related polymers which do not have 6F groups. Incorporation of the 6F groups into the polymer backbone produced easily soluble compounds while maintaining their high thermal stability and a large window between decomposition and glass transition temperature. Due to these groups, the present polymers also show outstanding capability to be processed into thin, colorless, flexible films or coatings, having a low dielectric constant. All these properties make these polymers potential candidates for high-performance applications, such as in microelectronics, optics, or related industries.

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