Poly(oxadiazole-amide)s containing hexafluoroisopropylidene

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A series of new poly(oxadiazole-amide)s that are soluble in polar solvents has been prepared by incorporating the hexafluoroisopropylidene unit and other flexible linkages into the backbone. Films cast of these polymers from solution are colourless to light tan and have ultimate tensile strengths ranging from 38.1 to 44.7 MPa. Weight loss does not occur below 450°C in air by thermogravimetric analysis and the inherent viscosities ranged from 0.31 to 0.42 dl g^{-1} in dimethylacetamide.

(Keywords: poly(oxadiazole-amide); polyoxadiazole; polyamide; polyhydrazide; 1,1,1,3,3,3-hexafluoroisopropylidene)

Introduction

Aromatic polyoxadiazole fibres and films are known to have a combination of good properties, such as thermal and hydrolytic stability, strength, stiffness, fatigue resistance, and a relatively low density. However, these polymers often have poor solubility in many solvents and are frequently processed from sulphuric acid solutions[1].

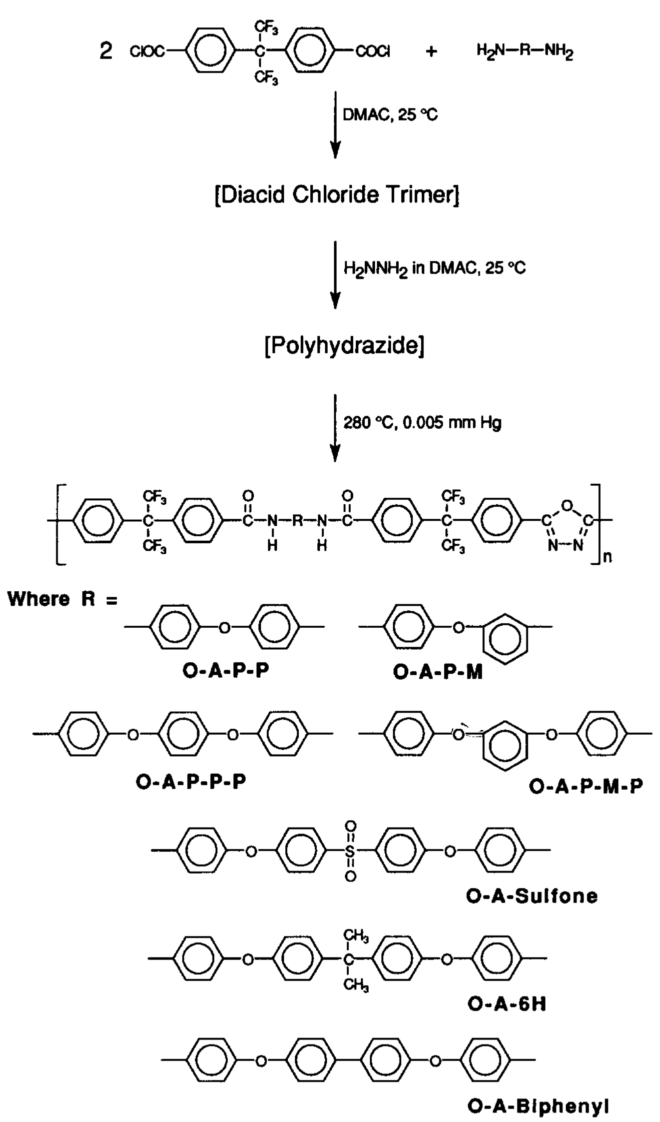
We have prepared a new series of polyoxadiazoles that have good solubility and still retain desirable mechanical and thermal properties by incorporating varied aromatic structures with flexible linkages into the polymer backbones. The linkages used are hexafluoroisopropylidene (HFIP), aromatic ether, sulphone and isopropylidene. Some of the properties attributed to the HFIP group when it is incorporated into a polymer backbone are an increase in solubility, flame resistance, thermal stability, oxidation resistance and glass transition temperature, while there is often a decrease in colour, crystallinity, dielectric constant and moisture absorption[2].

Experimental

Materials. The 2,2-bis(4-carboxyphenyl)hexafluoropropane (HFIP acid; Central Glass Co., Ltd), was obtained in 98% purity and recrystallized from glacial acetic acid, m.p. 273–275°C. Anhydrous hydrazine (Aldrich Chemical Co.) was 98% pure and was used as received. Thionyl chloride (Aldrich Chemical Co.) and anhydrous dimethylacetamide (DMAC, Aldrich Chemical Co.) were each >99% pure. The seven diamines (Kennedy & Klim, Inc.) were used without further purification: bis(4-(4-aminophenoxy)phenyl)sulphone, 98.58%; 2,2-bis(4-(4-aminophenoxy)phenyl)propane, 99.36%; 1,3-bis(4-aminophenoxy)benzene, 99.49%; 1,4-bis(4-aminophenoxy)benzene, 99.75%; 4,4-bis(4-aminophenoxy)biphenyl, 99.90%; 3,4'-diaminodiphenyl ether, 99.73%; 4,4'diaminodiphenyl ether, 99.86%.

Monomer synthesis. The 2,2-bis(4-chlorocarbonylphenyl)hexafluoropropane (HFIP acid chloride) was prepared by boiling 2,2-bis(4-carboxyphenyl)hexafluoropropane in thionyl chloride with a drop of pyridine. The product was recrystallized from a 1:1 mixture of benzene and hexane, and melted at 97.0°C[3].

General polymer synthesis. Scheme 1 illustrates the preparation of these polymers. The apparatus consisted



Scheme 1 Synthesis of the poly(oxadiazole-amide)s

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of a 100 ml, three-neck flask equipped with a magnetic stirrer, an argon purge and a $CaCl_2$ drying tube. The concentration of solids in each reaction ranged from 10 to 15% (w/v). A portion of the anhydrous DMAC was added to the flask with two molar equivalents of the HFIP acid chloride and was stirred rapidly at room temperature. The remainder of the DMAC was placed in an addition funnel with one molar equivalent of a diamine, which was added dropwise to the flask in order to favour the formation of a trimeric diacid chloride. The flask was then cooled to 0°C with an ice bath. A solution consisting of 0.0899 g of hydrazine (anhydrous) per 1.000 g of solution was prepared using DMAC as the solvent. One molar equivalent of the hydrazine solution was weighed out and added dropwise to the flask at 0°C. The solution was stirred at 0°C for 30 min after the last addition of monomer and then at room temperature for 3 h. The polyhydrazide was recovered by pouring the reaction mixture into methanol and purified by a solvent–non-solvent procedure using DMAC and water.

Cyclodehydration of the polyhydrazides. The polyhydrazides were cyclodehydrated to the oxadiazole structure by being heated in a vacuum oven from room temperature to 280°C over ~3 h, and then isothermally aged at 280°C under a 0.005 mmHg vacuum for a total heating time of 24 h. The polymers cyclize readily in the film and bulk forms and the resulting films are colourless to light tan and transparent.

Results and discussion

The acronyms of the polymers are shown in *Scheme 1*. In these structures, 'O-A' stands for 'oxadiazole-amide' and 'P' (*para*) or 'M' (*meta*) refer to the catenation of each ring within the diamine structures. For example, the polymer derived from 4,4′-diaminodiphenyl ether is given the acronym 'O-A-P-P' while other acronyms, such as 'O-A-sulphone', are self explanatory.

Table 1 lists the inherent viscosities of the polyoxadiazoles, which ranged from 0.31 to 0.42 dl g^{-1} when measured in DMAC at a concentration of 2.5 mg ml^{-1} at 25°C. Elemental analyses were generally in good agreement with their respective structures for hydrogen and nitrogen, while several of the carbon analyses were 1–2% below their theoretical values, a phenomenon common to high temperature heterocyclic polymers. Contributions to this low analysis are also likely to be incomplete cyclization and retaining of DMAC.

Cyclodehydration in the solid state has attracted much attention because of its simplicity and effectiveness[1]. High molecular weight polyoxadiazoles having wholly aromatic structures can be readily prepared by heating the polymer in the bulk or fibre form at 280°C while under nitrogen or a high vacuum for 3 to 48 h[4]. Polyhydrazides may also be cyclodehydrated by heating them in a strong dehydrating agent such as polyphosphoric acid or oleum[5].

The cyclodehydration of all the polyhydrazides was followed by infra-red (i.r.) spectroscopy using a Perkin-Elmer model 1600 *FT*i.r. The i.r. spectra of the thin polyhydrazide films showed carbonyl absorptions at 1635 and 1670 cm^{-1}. The film samples were then cyclodehydrated at 280°C and 0.005 mmHg for 24 h before their i.r. spectra were taken again, at which time only the 1670 cm^{-1} carbonyl peak attributed to the amide carbonyls remained. A reduction in absorbance at the amide N–H stretching near 3310 cm^{-1} was observed after cyclodehydration. The polyoxadiazoles were further characterized by their absorbance at 1520–1530 cm^{-1} that is attributed to the C–N stretch of C–NH and to the –NH interaction of bending. Absorptions were found near 1020 and 950 cm^{-1} that are characteristic of =C–O–C= stretching in the oxadiazole ring. Aromatic ether absorptions were found at 1220–1250 cm^{-1} and the sulphone absorption is at 1160 cm^{-1} for the O-A-sulphone polyoxadiazole.

Cyclization to the oxadiazole structure was also confirmed by ^1H n.m.r. spectroscopy using a Varian 200 MHz *FT*n.m.r. with deuterated dimethylsulphoxide as the solvent. The polymers showed their characteristic absorptions in the aromatic range and an amide hydrogen bonding peak at 10.5 ppm, which by integration agrees with their polyoxadiazole structures.

Thermogravimetric analyses of the polyoxadiazoles were performed with a duPont 9900 thermal analysis system at a heating rate of 20°C min^{-1}. Isothermal ageing was carried out in a Thermolyne type 1300 furnace. *Table 1* lists the thermogravimetric and isothermal data for the polyoxadiazoles. The polyoxadiazoles show an initial weight loss between 450°C and 471°C and a 10% weight loss between 486°C and 504°C in nitrogen and in air. It is interesting that, owing to the lack of an

Table 1 Polymer characterization

		Thermal stabilities in air		
Sample	Inherent viscosity (dl g^{-1})	Thermogravimetric analysis (°C)[a] T_0/T_{10}	Isothermal 300°C, % loss 100 h/300 h	Isothermal 350°C, % loss 100 h/300 h
O-A-P-P	0.42	457/486	6.83/9.90	26.72/50.38
O-A-P-M	0.33	455/487	6.19/12.13	8.27/67.62
O-A-P-P-P	0.37	451/488	11.52/22.16	50.04/86.05
O-A-P-M-P	0.40	450/494	9.12/12.25	13.15/68.08
O-A-sulphone	0.35	445/488	9.91/15.77	29.68/61.42
O-A-6H	0.43	471/504	6.20/19.17	51.55/68.60
O-A-biphenyl	0.31	466/502	4.44/9.42	20.40/67.50

[a] T_0 represents the initial weight loss temperature and T_{10} stands for the 10% weight loss temperature. All of the polyoxadiazoles show similar T_0s and T_{10}s in air and nitrogen

oxidatively susceptible function, the thermal stabilities in air and nitrogen are essentially identical, except for char yield.

In isothermal analyses all polymers, save two, behaved similarly at 300°C. But at 350°C two polymers proved to be superior at 100 h (O-A-P-M and O-A-P-M-P), indicating that phenyl ethers with some *meta* catenation seemed to be beneficial.

The analyses of the polyoxadiazoles by differential scanning calorimetry were performed in an inert atmosphere with a Perkin-Elmer model 2 thermal analyser at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. The polyoxadiazoles did not show a glass transition temperature prior to their decomposition.

All of the polymers are readily soluble in *N*-methylpyrrolidone, dimethylformamide, DMAC, dimethylsulphoxide, *m*-cresol, pyridine and concentrated sulphuric acid. All of the polymers swell when they are heated in tetrahydrofuran. The polyoxadiazoles swell in the solvent chloroform with the exceptions of O-A-P-P and O-A-biphenyl, which have the least bulky structures. The polyoxadiazoles O-A-P-M, O-A-P-P-P and O-A-P-M-P swell when heated in benzene.

The tensile strengths and related properties were obtained from samples in the form of thin films cast from DMAC. The initial moduli range from 119 to 188 MPa, the ultimate strengths are from 38.1 to 44.7 MPa, and the ultimate elongations range from 6.3 to 15.6%.

Moisture absorptions were determined by allowing a thin film sample to reach equilibrium by weight in deionized water at room temperature. Equilibrium was complete within 48 h and the moisture absorptions of the polyoxadiazoles are near 3.4%, while those of the polyhydrazides are around 4.5% by weight.

Conclusions

The enhanced solubility of the polymer structures resulting from the inclusion of HFIP and other linkages allowed their polymerizations to be carried out like a common polyamide synthesis in a polar aprotic solvent. The polymers cyclized readily in both the solid state bulk and film forms. The polyoxadiazoles formed light tan to colourless films having 10% weight losses around 500°C. We are continuing our polyoxadiazole work by investigating poly(oxadiazole-imide)s containing hexafluoroisopropylidene and silicon- and HFIP-containing polyoxadiazoles.

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