Fluorine- and silicon-containing polyoxadiazoles

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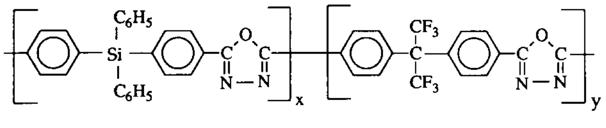
Colourless polyoxadiazoles containing both hexafluoroisopropylidene and diphenylsilyl groups in the backbone have been synthesized. The new film-forming polymers are soluble in common solvents (tetrahydrofuran, $CHCl_3$) and are stable (by thermogravimetric analysis) to about 500°C in both nitrogen and air.

(Keywords: hexafluoroisopropylidene; polyoxadiazole; silicon)

Introduction

Aromatic poly(1,3,4-oxadiazole)s represent a relatively unexploited class of thermally stable polymers[1]. They are most commonly prepared either by bulk cyclodehydration of a preformed polyhydrazide or by solution polymerization of dicarboxylic acids (or their derivatives) with hydrazine in the presence of dehydrating acids[2]. Although they form tough films and fibres, aromatic polyoxadiazoles are often coloured and are generally soluble only in sulfuric acid, trifluoroacetic acid or phosphoric acid[3]. However, polyoxadiazoles containing the 1,1,1,3,3,3-hexafluoroisopropylidene group (6F) have been reported to be soluble in common organic solvents[4]. Another report disclosed that the incorporation of the diphenylsilyl group into the polyoxadiazole backbone similarly led to soluble, colourless polymers[5]. The presence of both silicon and fluorine in a single polymeric material would be expected to give a material useful in aerospace applications (providing, for example, resistance to both u.v. radiation and atomic oxygen ablation), therefore a series of copolyoxadiazoles containing both the 6F and diphenylsilyl groups (compound **1**) was prepared.



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Experimental

Preparation of copolyhydrazides: 50% 6F/50% Φ_2Si. In a typical experiment, 2,2-bis(4-chlorocarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6F diacid chloride) (2.5000 g, 5.8255 mmol) and bis(4-chlorocarboxyphenyl)diphenylsilane (Φ_2Si diacid chloride) (2.6880 g, 5.8255 mmol) were dissolved in CH_2Cl_2 (291 ml) and cooled to 0°C. Hydrazine dihydrochloride (1.2231 g, 11.6523 mmol) was dissolved in 0.1 M KOH (466 ml) and placed in a Waring high-speed blender at 0°C. The mixture of diacid chlorides was then added to the rapidly stirring aqueous hydrazine solution, and stirring was continued for 10 min. The white copolyhydrazide was then isolated by filtration and was washed, first with acetone (300 ml), then with successive 100 ml portions[6] of CH_3OH, C_6H_6, CH_3COCH_3, H_2O, CH_3COCH_3, H_2O and CH_3COCH_3. The product was then dried *in vacuo* at 110°C for 12 h. Yield = 3.70 g (4.58 mmol, 79%).

The 25% 6F/75% Φ_2Si and 75% 6F/25% Φ_2Si were obtained in an analogous manner in yields of 84% and 87%, respectively.

Preparation of copolyoxadiazoles: 50% 6F/50% Φ_2Si. The powdered 50% 6F/50% Φ_2Si copolyhydrazide, which was first placed in an aluminium foil boat, was heated under vacuum (~26.7 Pa) for 4 h at 280–285°C and then for 12–14 h at 295–305°C. It was quantitatively converted to the white copolyoxadiazole, which was then dissolved in tetrahydrofuran (THF) and reprecipitated from methanol. The 75%/25% and 25%/75% 6F/Φ_2Si copolyoxadiazoles were prepared by a procedure identical to that described above for the title copolymer.

Discussion

Copolyoxadiazoles were prepared by thermal cyclodehydration of precursor copolyhydrazides containing both the 6F and the Φ_2Si groups in the backbone (*Scheme 1*).

Incorporation of the diphenylsilyl group into the backbone of the polyhydrazides and polyoxadiazoles was monitored by i.r. spectroscopy. I.r. bands at *c.* 735 and 700 cm^{-1}, arising from ring bending and out-of-plane wagging in the pendant phenyl groups, grow in intensity relative to other bands as the amount of the diphenylsilyl repeating unit is increased in the copolymer backbone. The cyclization reactions were

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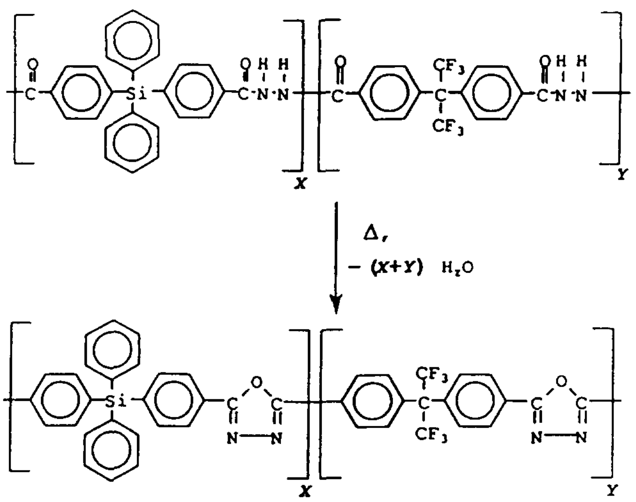

Where: X = 25%, Y = 75% } 6F/Φ_2Si copolyoxadiazoles
X = 50%, Y = 50%
X = 75%, Y = 25%
X = 0%, Y = 100% – 6F homopolyoxadiazole
X = 100%, Y = 0% – Φ_2Si homopolyoxadiazole

Scheme 1 Cyclodehydration of polyhydrazide to polyoxadiazole

Table 1 Polyhydrazide to polyoxadiazole cyclodehydration conditions

Polyhydrazide	Temperature (°C)	Time (h)
6F homopolymer	300	4
	310	4
	315	2
Copolymers		
75% 6F/25% Φ_2Si 50% 6F/50% Φ_2Si	280–285	4
25% 6F/75% Φ_2Si	295–305	12–14

carried out *in vacuo* at temperatures between 280 and 320°C. Thermogravimetric analysis (t.g.a.) results from the precursor polyhydrazides were used as a basis for determining the cyclodehydration temperatures. Invariably, temperatures higher than those shown in *Table 1*, even for short periods of time (2–3 h), resulted in degradation and decomposition of the polymers to a brownish-black mass, to loss of more than the stoichiometric mass required for cyclodehydration, and to insolubility of the product polyoxadiazoles in $CHCl_3$ and THF. Frazer and Sarasohn[7] have noted that the properties of the product polyoxadiazoles are influenced by the cyclization temperatures used. Cassidy and Fawcett[1] have suggested that cyclodehydration of polyhydrazides to polyoxadiazoles should be conducted at 25–50°C below the temperature observed for cyclodehydration by t.g.a. for extended periods of time instead of at higher temperatures for shorter times. The results in *Table 1* confirm this.

The solubility of the copolyoxadiazoles (in THF, $CHCl_3$, *N*-methylpyrrolidone (NMP) and dimethylacetamide (DMAC)) is greatly increased over that of the precursor polyhydrazides (very sparingly soluble in DMAC and NMP) with the polyoxadiazoles being very soluble in THF (up to 10% weight/volume solutions). This solubility difference allows the separation of small amounts of uncyclized polyhydrazide by extraction of the pyrolysis product with THF followed by reprecipitation of the pure polyoxadiazole from methanol. The presence of even small amounts of uncyclized polyhydrazide can be detected by i.r. bands at 3200 cm^{-1} ν(N–H) and 1650 cm^{-1} ν(C=O), which are of course absent in the polyoxadiazole.

Clear, flexible films of the new polyoxadiazoles are readily cast from THF. The u.v.–vis. spectra of the films confirm the absence of any absorption between about 350 and 800 mm. Strong absorption occurs below 350 mm. Analytical results and inherent viscosities are tabulated in *Table 2*. Analyses are consistently low in carbon, suggesting that the 6F moiety is preferentially incorporated into the polymers during the synthesis of the polyhydrazide precursors because of the difference in the reactivities of the 6F and Φ_2Si diacid chlorides to hydrazine. The copolyoxadiazole compositions derived from the analytical data are shown in *Table 2* (column 1).

There is also a decrease in inherent viscosity in going from the polyhydrazide precursor to the polyoxadiazole (*Table 2*). This decrease is expected as the strongly hydrogen-bonded polyhydrazide is converted to the non-hydrogen-bonded polyoxadiazole, although some of the decrease might be attributed to chain scission during the thermal cyclodehydration. In spite of the relatively low solution viscosities, all polyoxadiazoles form strong, flexible films.

T.g.a. results show similar thermal stability for the copolyoxadiazoles and the homopolymer analogues (*Table 3*). This is reasonable in that all backbones contain the same functional groups, but in different ratios. Remarkably, the oxidative stability is also excellent for all polymers with significant decomposition not occurring below 500°C (*Figure 1*).

Table 2 Results of C, H, N analyses and inherent viscosity measurements[a] for polyoxydiazoles

Polyoxydiazole composition: observed (planned)	Analysis (%): Exp. (Calc.) C	H	N	η^{*}_{inh}[b] (dl g^{-1})	η_{inh} (dl g^{-1})
87% 6F/13% Φ_2Si (75% 6F/25% Φ_2Si)	58.1 (61.1)	3.0 (3.0)	6.6 (7.4)	0.45	0.34
55% 6F/45% Φ_2Si (50% 6F/25% Φ_2Si)	65.3 (66.8)	3.9 (3.4)	6.7 (7.3)	0.48	0.25
30% 6F/70% Φ_2Si (25% 6F/75% Φ_2Si)	71.0 (72.3)	3.7 (3.9)	6.7 (7.1)	0.35	0.18

[a] All viscosities measured in DMAC at 25°C (0.25 g dl^{-1})
[b] Inherent viscosity of polyhydrazide precursor

Table 3 T.g.a. results for polyoxadiazoles

Polyoxadiazole	Decomposition temp. in N_2[a] (°C)	Decomposition temp. in air[a] (°C)
6F homopolymer[4]	524	520
75% 6F/50% Φ_2Si copolymer	504	498
50% 6F/50% Φ_2Si copolymer	499	495
25% 6F/50% Φ_2Si copolymer	530	513
Φ_2Si homopolymer[5]	530	510

[a] 10% weight loss, heating rate of 20°C min^{-1}

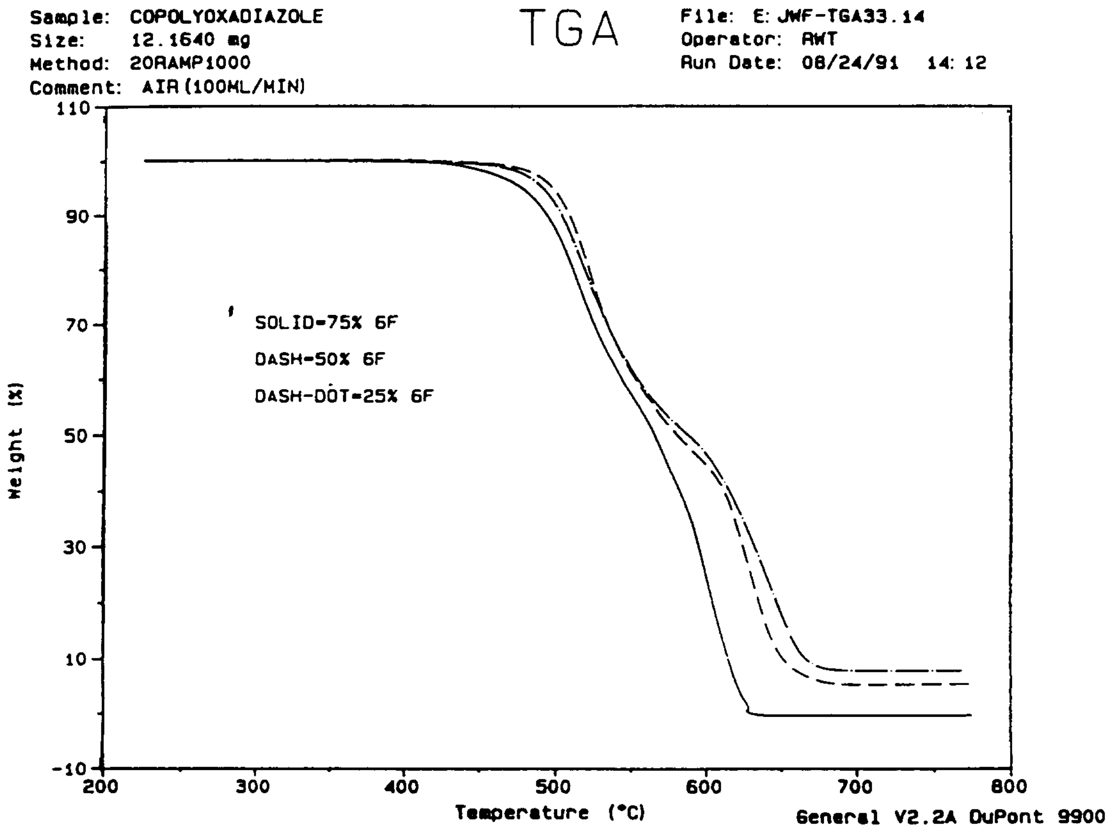

Figure 1 T.g.a. plots of 6F/Φ_2Si copolyoxadiazoles in air

Acknowledgements

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