Degradation of fluorinated polyoxadiazole in wet acidic media

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ABSTRACT

The chemical degradation of poly(2,5-(4,4'-(hexafluoropropylidene)diphenyl)-1,3,4-oxadiazole) (F-POD) was studied in wet acidic media using a variety of analytical techniques. It was found that in aqueous acidic solution, F-POD degradation increased with higher acidity (lower pH) and can reach levels of up to 20% in mild acidic conditions (pH 5.5). Furthermore, residual water present in chloroform was found to be capable of inducing degradation in the fluorinated polymer as well. A mechanistic explanation of the hydrolysis is proposed, which implicates the electron withdrawing effect of the hexafluoroisopropylidene group in the oxadiazole ring opening. The initially linear polymer is suggested to be transformed into a bi- or three-dimensional polymer (i.e., a branched or cross-linked structure) due to the attack of 1,3,4-oxadiazole ring by carboxylic hydrazide, causing a considerable loss of its solubility in organic solvents. Finally, we demonstrate that F-POD is susceptible to cross-link *via* relatively simple chemistry.

1. Introduction

Polyoxadiazoles (POD) are a class of hetero-aromatic polymers first reported in 1961 [1]. This class of polymers was developed during the cold war in the search for lightweight and thermal resistant materials for aerospace applications. Polyoxadiazoles are known to have high thermal and hydrolytic stability, strong mechanical properties and relatively low density [2–4]. The ability to form films and fibres with POD quickly gave rise to applications such as fabrication of heat-resistant fibres used in fire-retardant clothing [5,6]. In the recent decades, doped POD has also been used as an advanced material for organic electronics and optoelectronic applications [7]. This is due to the high charge and photoconductivity exhibited by these materials, which can be used for charge storage, electrochemical sensors and electroluminescent devices such as LED and OLED [7–10].

The properties of POD were especially impactful in the field of membrane science. In addition to being resistant to high temperatures, POD membranes are suited for harsh environments such as acids, bases and organic solvents [11]. Gas permeation membranes made from poly-1,3,4-oxadiazole can be tailored by the addition of functional groups to the polymer backbone to obtain a wide range of permeability and selectivity [12,13]. Polyoxadiazoles are also attractive to fuel cell applications when doped or sulfonated to increase proton conductivity [14–16]. In the presence of doping with phosphoric acid, the conjugated heterocyclic ring facilitates the transport of protons in proton electrolyte membrane fuels cells [14]. Membranes made of POD were also considered for reverse osmosis, but enjoyed limited success since

other polymeric membranes yield higher salt rejection capability [17,18]. Nevertheless, POD is considered as a substitute for ceramic membranes for processes requiring temperatures up to 300 °C, such as those used for catalysis, chemical synthesis, and other processes in the petrochemical and pharmaceutical industries [19].

Polyoxadiazoles are soluble only in certain acids, such as sulfuric, trifluoroacetic and phosphoric acids. The fluorinated polyoxadiazoles (F-POD), by virtue of the incorporated hexafluoroisopropylidene groups, are soluble in a wider range of organic solvents, allowing for easier processing into fibres and membranes [20]. It is also believed that the F-POD fibres have decreased combustibility [21]. The added hexafluoroisopropylidene groups in F-POD also increase the void spaces in the membrane matrix of gas permeation membranes, increasing permeability and selectivity [12,13]. Another interesting property of F-POD is its high hydrophobicity, which coupled with its high thermal stability, strong mechanical properties and ease of processability, make this polymer an attractive option for low-energy water treatment membrane processes [22–24].

In the past, F-POD was usually synthesized through condensation of hydrazine with dibasic acids in oleum, since thermal dehydration of perfluoropolyhydrazides was not possible due to decomposition [25,26]. Other synthetic routes included the cyclisation of poly-hydrazides and condensation of a diacid chloride with bistetrazole [26]. In recent years, an easier synthetic methodology was adopted to produce F-POD, which involved the condensation of a diacid with hydrazine sulfate using poly(phosphoric) acid as solvent and dehydrating agent [27,28].

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Although POD is considered to be very chemically stable, the hydrolysis of POD is known to occur, leading to the opening of the 1,3,4-oxadiazole ring in the presence of acids [3,29]. In this work, a similar mechanism is detected in F-POD. The electron withdrawing effect of the hexafluoroisopropylidene group weakens the carbon bonds in the oxadiazole ring, leading to a further degradation of the molecule through hydrolysis in acidic media. The vulnerability of F-POD is demonstrated in different acidic media, along with how this degradation property can be explored as a method to crosslink the polymer.

2. Experimental

2.1. Materials

The synthesis of F-POD is reported elsewhere [19,28]. Acetic acid (Sigma Aldrich, USA, > 99.8%), hydrochloric acid (Fisher scientific, USA, 37%), deuterated chloroform ($CDCl_3$) (Merck Sharp and Dohme, Montreal, > 99.8% D), deuterated dimethylsulfoxide (DMSO-d_6) (Wilmad Glass Co., USA, > 99.8% D), tetrahydrofuran (THF) (Sigma Aldrich, USA, > 99.9%), hexylamine (Sigma Aldrich, USA, 99%), 1,8-diaminooctane (Sigma Aldrich, USA, 98%) and iron sulfide (Sigma Aldrich, USA, > 95%) were used without further purification. Ultra-pure water was purified on a Milli-Q® Integral 15 water system.

2.2. F-POD degradation

2.2.1. Aqueous acidic F-POD degradation (pH 1.5 & 5.5)

A small sample of F-POD (25 mg) was added to 20 mL of an aqueous solution of hydrochloric acid (31.7 mmol/L) and acetic acid (872.5 mmol/L). The pH of the solution was 1.5. Another F-POD sample was added to 20 mL of an aqueous solution of hydrochloric acid (31.7 mmol/L) and iron sulphide (187.1 mg, 2.13 mmol). The pH was 5.5. Both mixtures were left overnight at 25 °C. The treated F-POD samples were then rinsed with pure water and left to dry overnight. Both samples were analysed by differential scanning calorimeter (DSC), thermogravimetric analyser (TGA) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR FTIR) spectroscopy. The average molecular weights of the samples were subsequently determined using gel permeation chromatography (GPC).

2.2.2. Non-aqueous acidic F-POD degradation

An F-POD sample (25 mg) was added to 1 mL of $CDCl_3$. This liquid mixture was analysed by NMR spectroscopy immediately after dissolution and by FTIR spectroscopy after being left overnight at 25 °C. The remaining solution was left to evaporate at 25 °C. The resulting beige solid was not soluble in $CDCl_3$. The solid was partially dissolved at 60 °C in DMSO-d_6 and was analysed again by NMR spectroscopy.

2.2.3. Reaction of F-POD with hexylamine

An F-POD sample (23.1 mg) was added to 1 mL of a deuterated chloroform solution with 29.2 mg (286 μmol) of hexylamine. The mixture was left overnight at 25 °C. An off-white solid precipitated immediately. This precipitate was analysed by FTIR and NMR spectroscopy in DMSO-d_6.

2.2.4. Crosslinking reaction of F-POD

An F-POD sample (26.2 mg) was added to 1 mL of a deuterated chloroform solution with 1.8 mg (12.2 μmol) of 1,8-diaminooctane. The mixture was left overnight at 25 °C. An off-white solid precipitated immediately. This precipitate was analysed by FTIR and NMR spectroscopy in DMSO-d_6.

2.3. Analytical methods

2.3.1. NMR spectroscopy

Samples for NMR were prepared by dissolving the solid material in either $CDCl_3$ or DMSO-d_6. For DMSO-d_6 samples, heating at elevated temperatures was employed at times to homogenize the sample. All spectra were acquired on a *Varian 500 MHz NMR* spectrometer, equipped with a 5 mm liquids probe. The ^{1}H NMR spectra were acquired with a single 90° pulse, a 60 s recycle delay and a 5 s acquisition time. Generally, a line broadening of 0.5 Hz was applied to the FID before Fourier transformation. The spectra were typically calibrated to the TMS signal (0 ppm).

2.3.2. FTIR spectroscopy

Samples for FTIR were analysed as received in solid form. For the sample dissolved in $CDCl_3$, the solvent was evaporated prior to the test. FTIR spectroscopic data were collected for all samples using a *Varian FT-IR* spectrophotometer equipped with mercury cadmium telluride (MCT) detector and Golden gate accessory with an average of 128 scans at a resolution of 4 cm^{-1}.

2.3.3. Gel permeation chromatography

Samples for GPC were prepared by dissolving the solid material in THF (2 mg/mL). The samples were left for 30 min to ensure complete dissolution and then filtered through a 0.45 μm syringe filter prior to injection of 100 μL. The *Agilent 1260 Infinity GPC/SEC* system was equipped with a degasser, an isocratic pump, an autosampler, a thermostatted column compartment and a refractive index detector. The pump was used to achieve a THF eluent flow rate of 1 mL/min through two GPC columns (type 100 Å and 10,000 Å), each 30 cm long and connected in series. The columns were packed with highly cross-linked polystyrene-divinylbenzene (*Phenogel^{TM}*) 5 μm particles. The temperature of the column oven was maintained at 30 °C. Calibration was achieved using *Agilent EasiCal* polystyrene standards (molecular weights: 580; 1390; 2780; 4830; 9970; 19,540; 51,150; 113,300; 224,900 and 483,400 g/mol) dissolved in THF. The average molecular weight of the samples was calculated from the plot of molecular weight versus relative retention time, using the integrated *Agilent* software.

2.3.4. Differential scanning calorimeter

Glass transition temperatures were determined by a *TA instruments DSC Q20* coupled with refrigerated cooling system, following ASTM D3418 standard method. Scans were run with 5 mg of sample under a nitrogen purge (20 cm^3/min) as follow a heating cycle at a heating rate of 10 °C/min to 400 °C, a cooling cycle at a rate of 100 °C/min to 20.0 °C, and finally a heating cycle at a heating rate of 10 °C/min to 400 °C. Reported values were obtained from a second heating run.

2.3.5. Thermogravimetric analysis

The samples were analysed using a *TA instruments TGA Q500* that was programmed to run at a heating rate of 10 °C/min between 20 °C and 800 °C under a nitrogen atmosphere to determine the weight losses of the samples. About 5 mg of each sample was uploaded into TGA sample pan.

3. Results & discussions

The water-insoluble poly(2,5-(4,4'-(hexafluoropropylidene)diphenyl)-1,3,4- oxadiazole) (F-POD in Fig. 1) was exposed to acidic aqueous solutions (pH 1.5 and 5.5). In parallel, a similar amount of F-POD was added to pure water as a reference sample.
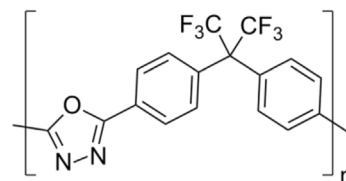

Fig. 1. F-POD chemical structure.