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Short communication

Novel fluoropolymers formed by an unprecedented $S_{RN}1$ condensation polymerization mechanism

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ABSTRACT

A condensation copolymerization reaction between bis-phenol A and *p*-bis-(chlorodifluoro-methyl)-benzene has been carried out to form a novel fluoropolymer that has excellent thermal and solubility properties. It is proposed that this polymerization reaction occurs via an unprecedented $S_{RN}1$ mechanism. This demonstration of the use of $S_{RN}1$ chemistry for condensation polymerizations of fluorinated monomers creates the opportunity for preparation of new fluoropolymers which are otherwise inaccessible.

1. Introduction

p-Bis-(chlorodifluoromethyl)benzene (**1**) is the precursor of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (AF4) [1], which itself is the CVD precursor of a highly thermally stable thin film Parylene polymer [2,3], which forms via *p*-xylylene monomer (**2**) (Scheme 1).

Unfortunately, when monomer **2** is generated in solution by various means it forms an insoluble, amorphous polymer that has no commercial value. Because of the generally strong bonds of most atoms to CF_2 groups, we considered it of interest to attempt the preparation of copolymers of monomer **2** using its dichloride precursor 1 as a substrate in a condensation polymerization process. However, our own experience and knowledge of the literature told us that compounds bearing a CF_2X group are *not* good substrates for S_N2 nucleophilic substitution reactions. Indeed, we have found that dichloride **1** will not react with excellent nucleophiles, such as cyanide ion (HMPA/130 °C) or azide ion (HMPA/60 °C).

On the other hand, additional experience we had with dichloride **1** indicated that it *would* react quite will with a good $S_{RN}1$ nucleophile such as phenyl thiolate anion, and even phenolate anion to give bis-adducts in very good yield (Scheme 2) [4,5]. On the basis of this experience, and in spite of the acknowledged complex free radical chain/SET mechanism of $S_{RN}1$ processes [6], we decided to determine whether a bis-phenolate or bis-thiolate monomer might be able to take part in a condensation polymerization process with monomer **1**.

2. Results and discussion

Indeed, after some optimization of conditions, bis-phenol A was found to act as an effective comonomer in the copolymerization of dichloride **1**. A yellow solid was obtained in 81% yield, the structure of which was assumed to be **5** (Scheme 3). The solid state fluorine NMR spectrum of the product (Fig. 1) exhibited a single major signal in the region of the spectrum which would be consistent with the Ar–CF_2–O– group present in **5**, the simplicity of the spectrum also indicating it to be a polymer of relatively uniform structure. The relative lack of signal in the CF_2H end group region (~130 ppm) was consistent with the 36,300 molecular weight (M_w) determined for the polymer by gpc, with M_n being 21,400. M_w/M_n thus has a value of 1.7 for polymer **5**. As would be expected for a condensation polymerization process, the M_w increased to 50,000 when the concentration of dichloride monomer was increased from 15 to 20%.

The T_M value for the polymer was 240 °C, and TGA experiments determined that it had good thermal stability in the liquid phase (10 wt.% loss at 335 °C) (Fig. 2). DSC experiments showed a transition peak at about 234 °C during the first heat. Upon cooling and second heat, a sharp transition was observed at 240 °C, seemingly followed by decomposition, such results being consistent with the TGA results.

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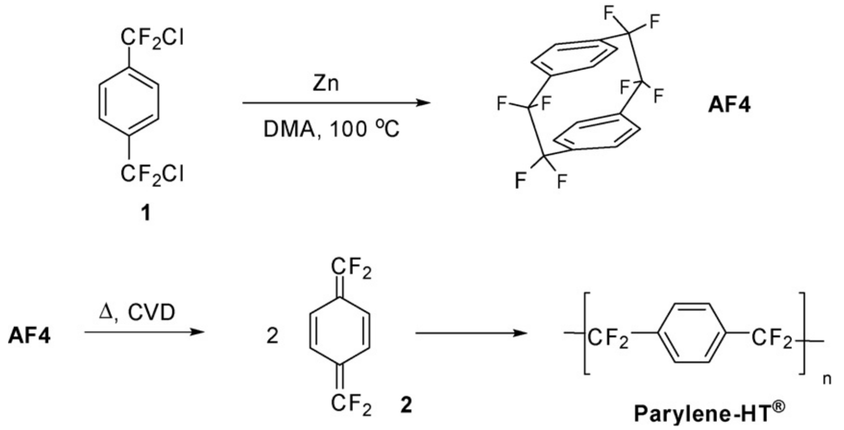
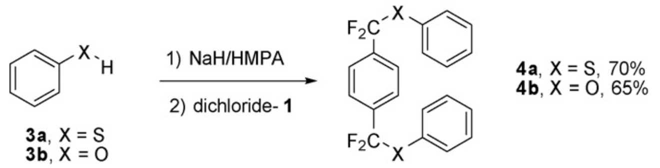
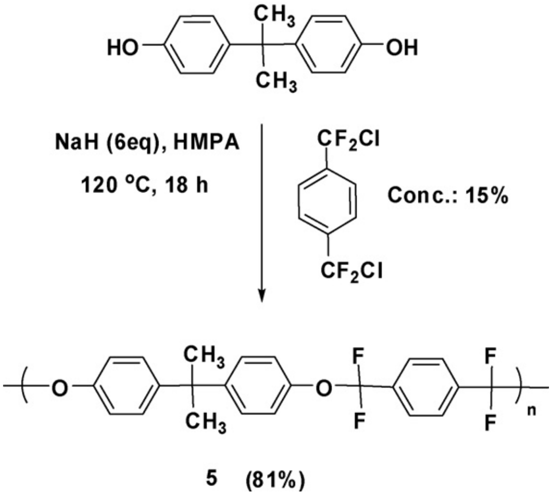


Scheme 1.



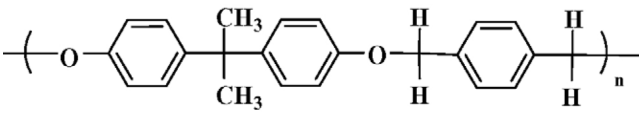
Scheme 2.



Scheme 3.

Polymer **5** also has good solubility characteristics, with 10 mL of DMSO dissolving 6 g at 180 °C.

That the presence of the fluorine substituents is enhancing the thermal stability of the polymer is indicated by a comparison of polymer **5** with the analogous fluorine free polymer, **6**, for which a "maximum of polymer degradation temperature", PDT of 350 °C was reported [7]. The PDT value of polymer 5 is 530(±20) °C.



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To our knowledge, an $S_{RN}1$ mechanism has never previously been invoked for a polymer forming process [8–11]. That the mechanism of the above polymerization process is almost certainly $S_{RN}1$, was first indicated by the earlier mentioned result that dichloride monomer **1** was unreactive with CN^- and N_3^- under conditions where phenoxide and thiophenoxide reacted smoothly. $S_{RN}1$ processes are known to be enhanced by light and inhibited by the presence of O_2. Indeed, the model reaction of dichloride monomer with phenoxide ion in HMPA at 120 °C normally reaches 70% conversion after about 12 h, whereas when the reaction was irradiated by a sunlamp, 70% was attained in less than 3 h. With bubbling O_2, 70% was attained only after about 30 h. Lastly, when the "normal" thermal model reaction of phenoxide with dichloride monomer **1** was stopped after 2 h and the reaction mixture examined by EPR, a spectrum was observed that was consistent with that which would be expected for the radical anion of dichloride **1**, a quintet derived from coupling to four equivalent hydrogens (Fig. 3). The observed spectrum was very similar in structure to that reported for the radical anion of *p*-xylene [12,13].

Polymers of similar nature and quality were obtained using a number of other bis-phenolate and bis-thiolate comonomers, including 4,4′-dihydroxybenzophenone, 4,4′-dihydroxybiphenyl, and 1,3-propane dithiol, the properties of which will be reported in due course.

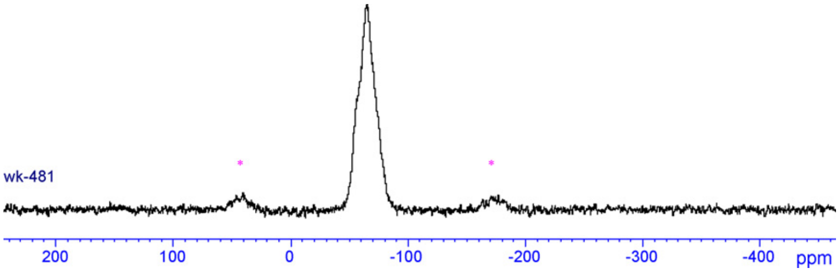

Fig. 1. ^{19}F NMR spectrum (solid state) of polymer **5**.

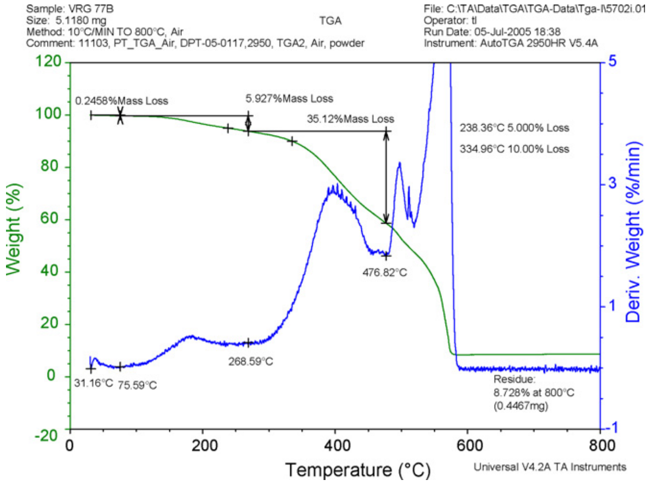

Fig. 2. TGA of polymer **5**.

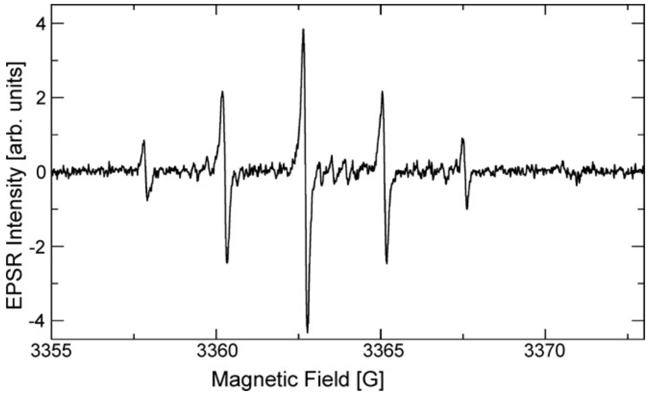

Fig. 3. EPR spectrum of probable radical anion of dichloride **1**.

In conclusion, novel fluoropolymers with potentially interesting properties can be prepared from 1,4-bis-(chlorodifluoromethyl)benzene via an unprecedented $S_{RN}1$ condensation polymerization process.

3. Experimental

3.1. Preparation of polymer 5

Bis-phenol A (0.46 g, 2.0 mmol), *p*-bis-(chlorodifluoromethyl)-benzene (0.50 g, 2.0 mmol) [14], NaH (95%, 0.29 g, 12.1 mmol) and hexamethylphosporamide (anhydrous, 8 mL) were added to a 25 mL round bottomed flask. The reaction mixture was stirred at 120 °C under N_2 overnight. After the reaction mixture was cooled to room temperature, it was added to water (100 mL) dropwise with stirring. One molar HCl was added to the solution until pH 1–2. The precipitate was then collected and washed by water (50 mL), acetone (10 mL) and ethanol (10 mL). It was then dried by a flow of N_2 to give a yellow solid (0.671 g, 87%).

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