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Synthesis and electrochromic properties of novel aromatic fluorinated poly(ether-imide)s bearing anthraquinone units

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ABSTRACT

A novel class of fluorinated poly(ether-imide)s (PEIs) with anthraquinone (AQ) units were prepared from the polycondensation reactions of a newly synthesized AQ-dietheramine monomer, namely 2,6-bis(4-amino-2-trifluoromethylphenoxy)-anthraquinone, with aromatic tetracarboxylic dianhydrides via a conventional two-step technique. The fluorinated polyimides exhibited enhanced solubility and optical transparency because of increased free volume caused by the CF_3 substituents. Furthermore, the PEIs showed high thermal stability, with glass-transition temperatures of 263–312 °C and decomposition temperatures in excess of 500 °C. These PEIs were also investigated by cyclic voltammetry and spectroelectrochemistry. Preliminary results reveal that these AQ-based PEIs are potentially useful as cathodically coloring red electrochromes.

1. Introduction

Aromatic polyimides are well-known as high performance polymeric materials that have excellent thermal stability and mechanical properties as well as good chemical resistance [1–5]. They are commercially important materials used extensively as military, aerospace, machine-building, electronics, etc. The outstanding properties of aromatic polyimides come from their rigid backbones and strong intermolecular forces between the polymer chains due to the charge transfer complex formation between electron-donating and electron-accepting segments. However, rigidity of the backbone and strong interchain interactions result in high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents. Thus, polyimide processing is generally carried out via poly(amic acid) precursor and then converted to polyimide by thermal or chemical cyclodehydration. This process has inherent problems such as emission of volatile by products and storage instability of poly(amic acid) solution. To overcome these problems, many attempts have been made to the synthesis of soluble and processable polyimides in fully imidized form while maintaining their excellent properties [6–8]. The majority of methods used for improving the solubility while maintaining the excellent performance of polyimides have involved the structural modifications of dianhydride and diamine monomers. Typical approaches include the introduction of flexible linkages, kinked or unsymmetrical structures, bulky packing-disruptive units and bulky lateral groups into the polymer backbone [9–13]. The incorporation of bulky CF_3-substituents into the polyimide backbone is well known to enhance the solubility and optical transparency of polyimides due to low polarizability of the C–F bond and the increase in free volume [14–18]. Furthermore, poly(ether-imide)s (PEIs) have received great attention because they may provide good processability owing to the presence of flexible ether linkages [19,20]. The development of a large class of PEIs from bis(ether amine)s and various aromatic dianhydrides or bis(ether anhydride)s which exhibit reasonable thermal stability and good mechanical properties together with good moldability [21–26].

On the other hand, incorporation of specific functionality into the polyimide backbones leads to various advanced functional materials that exhibit certain advantageous properties, such as electrochromic [27], gas separation [28], highly refractive [29], photosensitive [30], proton-conducting [31], and memory characteristics [32]. The studies in the field of functionalization of polyimides continue to be actively developed, as is evidently from the appearance of a large number of publications on this subject in the past few years. The widespread occurrence of quinones in nature and their importance in electron transport have led to extensive studies of their electrochemical behavior [33]. Anthraquinone (AQ) units are electron acceptor groups that have proved to be suitable receptors in colorimetric and fluorimetric sensors [34]. Besides, it has been demonstrated that a certain AQ

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system can be reversibly switched electrochemically from cross-conjugated (low conductance ‘off’) to linear conjugated (high conductance ‘on’) via two-electron reduction/oxidation reactions. This feature holds promise for AQ-based wires to be used as redox-controlled switches in molecular electronic devices [35]. Furthermore, some AQ derivatives and polymers have been reported to be candidates as redox-active and near-infrared (NIR) electrochromic materials because they exhibit intense NIR absorptions when the AQ units are electrochemically reduced to a radical anionic state or a dianionic state [36–38]. Recently, we have reported the synthesis of cathodically electrochromic AQ-containing polyimides from 2, 6-bis(4-aminophenoxy)anthraquinone and aromatic dianhydrides [39]. However, unless flexible dianhydrides were incorporated, the polyimides showed a limited solubility. For further enhancing the processability of this kind AQ-based polyimides, this study describes the synthesis of a new CF_3-substituted dietheramine, 2,6-bis(4-amino-2-trifluoromethylphenoxy)-anthraquinone **(3)**, and its use for the preparation of soluble PEIs by the reaction of the diamine with commercially available aromatic dianhydrides. These fluorinated PEIs were expected to exhibit enhanced solubility because of increased free volume caused by the bulky CF_3 substituents. In addition to basic characterization, the thermal properties and electro-optical properties of these PEIs will also be investigated.

2. Results and discussion

2.1. Monomer synthesis

2,6-Bis(4-amino-2-trifluoromethylphenoxy)anthraquinone **(3)** was synthesized starting from 2,6-dihydroxyanthraquinone **(1)** by a two-step reaction sequence as shown in Scheme 1. The intermediate dinitro compound **2** was prepared by the nucleophilic aromatic chloro-displacement reaction of 2-chloro-5-nitrobenzotrifluoride with AQ-diol **1** in the presence of potassium carbonate (K_2CO_3). Then, the target AQ-dietheramine monomer **3** was prepared by hydrazine Pd/C-catalyzed reduction of dinitro compound **2**.

The FT-IR spectra of all the synthesized compounds are shown in Supporting information (Fig. S1). The IR spectrum of the starting AQ-diol **1** gives rise to a broad absorption at about 3300–3500 cm^{-1} (–OH stretch). The intermediate dinitro compound **2** shows the characteristic absorption of nitro groups at around 1533 and 1315 cm^{-1} (–NO_2 asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared and the amino group shows the typical N–H stretching absorption pair at 3490 and 3374 cm^{-1} as shown in the IR spectrum of AQ-dietheramine **3**. The spectrum of **3** also exhibits a conjugated ketone stretching frequency at 1670 cm^{-1} and medium to strong C–F, C–N and C–O stretches in the region from 1400 to 1000 cm^{-1}.

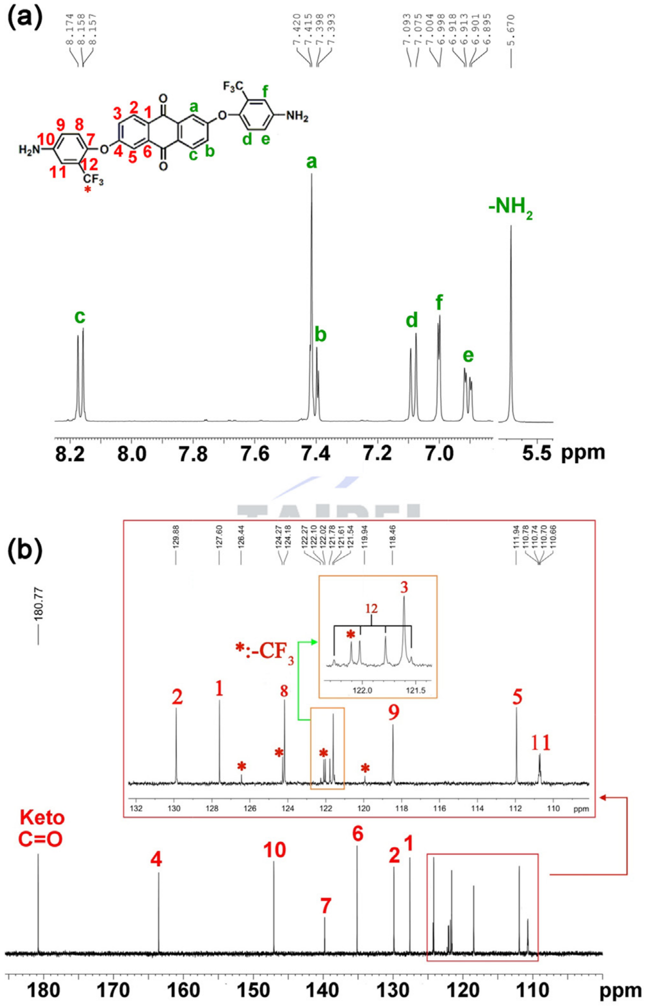
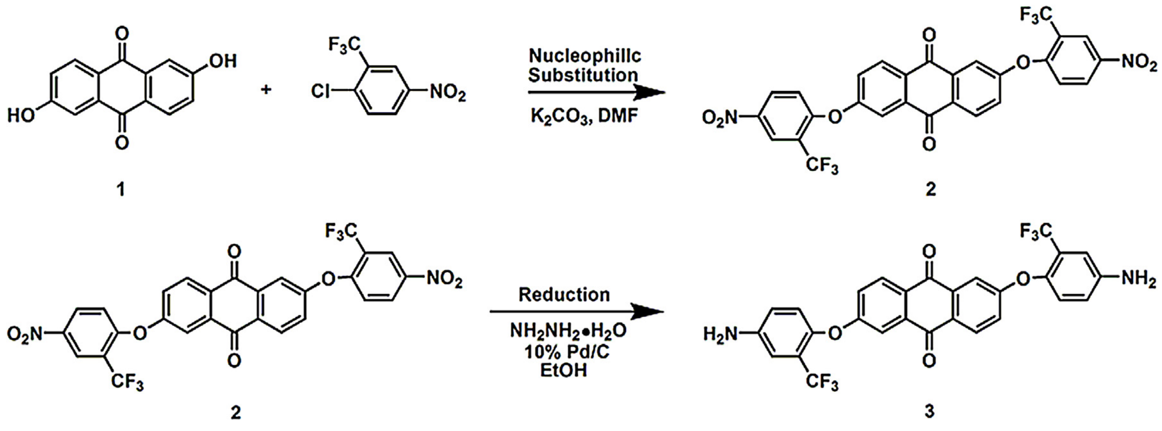


Fig. 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of AQ-dietheramine **3** in DMSO-d_6.

The ^1H, ^{13}C NMR, H–H COSY and C–H HMQC spectra of AQ-dietheramine **3** are compiled in Figs. 1 and 2, respectively. The ^1H NMR spectrum confirms that the nitro groups have been



Scheme 1. Synthetic route to the CF_3-substituted AQ-dietheramine monomer **3**.