Journal of Fluorine Chemistry 132 (2011) 878–884

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Optical and thermal behavior of novel fluorinated polyimides capable of preparing colorless, transparent and flexible films

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ARTICLE INFO

Article history:
Received 9 April 2011
Received in revised form 13 June 2011
Accepted 16 June 2011
Available online 23 June 2011

Keywords:
Fluorinated polyimides
Absorption edge
Heat resistant polymer
Trifluoromethyl
Gel-permeation chromatography
Differential scanning calorimetry

ABSTRACT

A new diamine, 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) was synthesized by the nucleophilic substitution reaction of 1,5-dihydroxynaphthalene and 4-chloro-3-nitrobenzotrifluoride in the presence of potassium carbonate in *N*,*N*-dimethylformamide, followed by catalytic reduction with hydrazine and Pd/C in ethanol. DA1524 was then utilized to prepare a novel class of CF_3-containing polyimides. Intrinsic viscosities [η] of the polymer solutions at 25 °C were measured by the extrapolation of their viscosity numbers till zero concentration. $\bar{M}_w$ and $\bar{M}_n$ values of the resulting polymers were determined using gel-permeation chromatography (GPC). The polymers showed a good film-forming ability, and some characteristics of their thin films including color and flexibility were investigated qualitatively. In addition, the absorption edge values (λ_0) obtained from their UV–vis curves were determined, and all the resulting polyimides films exhibited high optical transparency. Thermal stability of the polymers was investigated using TGA analyses. The T_g values of the polyimides obtained from their DSC plots were quantified. Solubility of the samples in a variety of organic solvents was also tested.

1. Introduction

Fluoro-containing polymers constitute a unique class of materials with a combination of interesting properties that have attracted significant attention of material chemists over the last few decades. In general, these polymers have high thermal stability, improved chemical resistance and lower surface energy when compared to their non-fluorinated counterparts [1–6]. On the other hand, for many applications, polymers need to have good film-forming ability, high chemical resistance, adequate organo-solubility and great thermo-stability. In order to answer these requirements, structural modifications of polymers often become essential. It has been observed that introduction of bulky substituents in preferably asymmetric backbones can impart many of these desirable properties to the polymers, making them suitable for a much wider range of applications [7–11]. Furthermore, aromatic ether linkages inserted in polymer main chains provide them with significantly lower energy of internal rotation. Such a structural modification leads to a lower glass-transition temperature (T_g) and crystalline melting temperature as well as a significant improvement in the solubility and process characteristics without greatly sacrificing thermal stability [12–16].

In 2004, a naphthalene-based bis(ether amine) monomer containing trifluoromethyl groups namely 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (DA1542) was synthesized by Hsiao et al. [17]. In a continuation of this study, in 2009, the isomeric form of diamine DA1542 namely 1,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (DA1742) was also synthesized by the same group [18]. Each of these monomers was then utilized to prepare the corresponding fluoro-containing polyimides. With due regard to noticeable role of polyimides in development of high performance materials, as well as their extensive application in advanced technologies, we decided to continue and modify the above interesting research area. Thereby, since it is well accepted that bond orientation and consequently macromolecular alignment has so much importance in good designing the structure of a new monomer, we thought that if 4-chloro-3-nitrobenzotrifluoride is used instead of its isomers, i.e. 2-chloro-5-nitrobenzotrifluoride in the reaction with dihydroxynaphthalene, the resultant monomer profit by more degree of asymmetry. In this case, both amino groups of the monomer were placed at the structure middles, not terminals. This could be surely resulted in the preparation of polyimides with high organo-solubility and better film quality. In addition, with a view to cost and availability, it seems likely that 1,5-dihydroxynaphthalene to be a better choice comparing its 1,7-isomer without noticeable lessening degree of asymmetry. Consequently, synthesis of 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) instead of diamines DA1542 and DA1742, as well as

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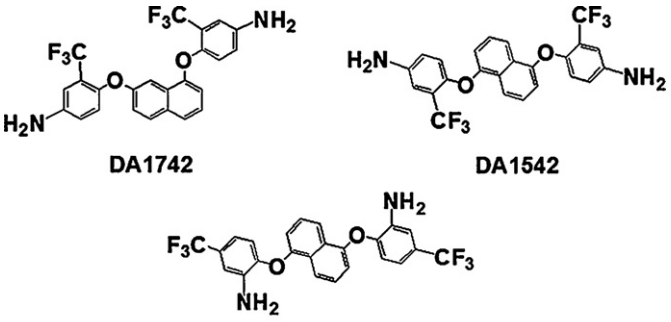
doi:10.1016/j.jfluchem.2011.06.017

preparation of the related polyimides via the polycondensation reaction of diamine DA1524 and various commercially available tetracarboxylic dianhydrides could be a good goal in our path. Indeed, the CF_3-substituted monomer 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) has two well-oriented amino groups that can endow its derivative polymers some desired properties like enhanced organo-solubility.



Accordingly, this work deals with the preparation of a series of new fluorinated polyimides derived from structurally well-designed diamine DA1524 and some dianhydride comonomers using a two-stage process with chemical imidization method. Optical and thermal behaviors of the obtained polymers are fully investigated and compared with those of previously reported counterparts. Film-forming ability and organo-solubility are the other topics that discussed in detail.

2. Results and discussion

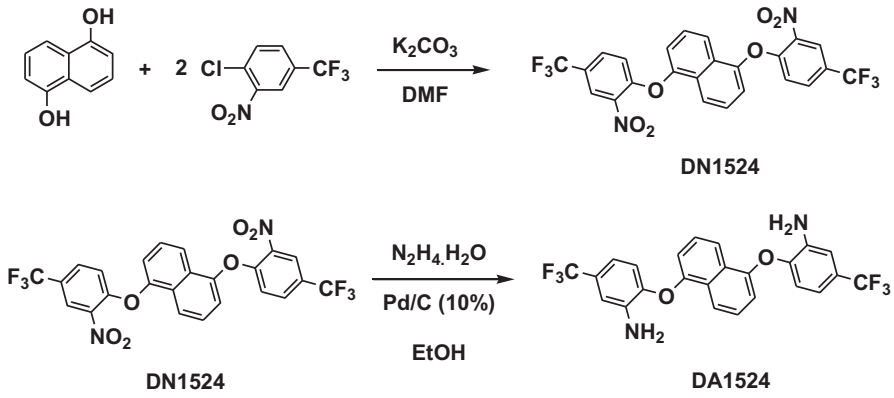
2.1. Synthesis processes

2.1.1. Dinitro DN1524 and monomer DA1524

Scheme 1 shows the synthesis route used to prepare 1,5-bis(2-amino-4-trifluoromethylphenoxy)naphthalene (DA1524) by a two-step process. In the first step, aromatic nucleophilic displacement of 4-chloro-3-nitrobenzotrifluoride with 1,5-dihydroxynaphthalene in the presence of anhydrous K_2CO_3 in DMF solvent resulted in the dinitro DN1524 as a yellow solid. In the second step, this dinitro intermediate was reduced in ethanol in the presence of hydrazine hydrate and a catalytic amount of palladium on activated carbon at 80 °C to produce white fine crystals of the new fluorinated diamine DA1524. The structures of dinitro DN1524 and diamine DA1524 were confirmed by IR and NMR spectroscopic methods. In the IR spectrum of dinitro DN1524, the peaks attributed to the stretching vibrations of the bond Ar–O appeared at 1265 cm^{-1}. Moreover, absorptions appearing around 1322 and 1540 cm^{-1} are due to symmetric and asymmetric stretching of $-NO_2$ groups. In the ^1H NMR spectrum of DN1524 all the existing signals can be easily attributed to their appropriate hydrogens in the chemical formula. Furthermore, in the ^{13}C NMR spectrum, 12 peaks corresponding to the 12 kinds of carbons appeared in the range 117.9–153.7 ppm. In this spectrum, the quartets of the heteronuclear ^{13}C–^{19}F coupling appeared in the region of 119.0–125.6 ppm with coupling constant of about 230 Hz. Thereby all these spectral patterns are thoroughly in agreement with the proposed structure of dinitro DN1524. In the IR spectrum of monomer DA1524, the characteristic absorption of nitro groups disappeared and the characteristic bonds of amino groups at 3439 and 3366 cm^{-1} (N–H stretching) and 1595 cm^{-1} (N–H bending) appeared after reduction. In the ^1H NMR spectrum of diamine DA1524, the signals of aromatic protons appeared in the range of 6.70–8.00 ppm. The characteristic resonance signal at 5.56 ppm is due to hydrogens of the amino groups. In the ^{13}C NMR spectrum of diamine DA1524, the quartets of the heteronuclear ^{13}C–^{19}F coupling appeared in the region of 120.0–126.8 ppm. Here, the coupling constant of one-bond C–F was found to be about 280 Hz. The results obtained clearly confirm that the structure of diamine DA1524 is consistent with that of the proposed structure.

2.1.2. Fluorinated polyimides

The ether-hinged fluorinated polyimides, i.e. DA1524/PMDA, DA1524/BTDA, DA1524/ODPA, and DA1524/6FDA were prepared by two-step polyimidization method involving ring-opening polyaddition of the reactants, leading to the appropriate poly(amic-acid) intermediate and subsequent cyclodehydration [19,20]. Scheme 2 outlines the synthesis route to the above polymers. In general, the cyclodehydration step can be done both thermally by heating an appropriate solution of the previously separated poly(amic-acid) and chemically by addition of some dehydrating agents such as a mixture of acetic anhydride and pyridine to the reaction system [21–23]. It is noticeable that thermal imidization method is not suitable for preparing polymers with high molecular weights since the chains may break in some points at high temperatures needed for thermal cyclodehydration step. This leads to lower values of solution viscosity. Therefore if possible (if a clear solution and not a suspension create during the polymerization reaction) chemical polyimidization using a dehydrating agent is better than the former method. Accordingly, in the current work, chemical cyclodehydration has been utilized to prepare the polymers. All the polycondensations were homogeneously throughout the reactions and afforded highly viscous polymer solutions with up to 95% yield. Intrinsic viscosity [η] values of the resulting polyimides in DMAc at 30 °C as well as the results of GPC analyses are tabulated in Table 1. Intrinsic viscosity values of the



Scheme 1. Synthesis of new monomer DA1524.