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Thickness dependent thermal rearrangement of an *ortho*-functional polyimide

Huan Wang [a], Tai-Shung Chung [a], D.R. Paul [a,b,*]

[a] *Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore*
[b] *Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA*

ABSTRACT

The effect of film thickness on the thermal rearrangement of an *ortho*-functional polyimide, derived from 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB), to a polybenzoxazole structure was explored over the range from 50 nm to 100 μm. The rate of thermal rearrangement of this *ortho*-functional polyimide was found to be strongly dependent on film thickness. A thin film of 56 nm experienced a much more rapid and extensive thermal rearrangement process than a thick film of 100 μm as tracked by thermogravimetric analysis, TGA. The conversion of the *ortho*-functional polyimide to polybenzoxazole commences at a lower temperature for thinner films than for thicker films. Isothermal TGA experiments at 370 °C showed a much larger weight loss, or extent of rearrangement, at a given time for thin films compared to thick films. These observations are believed to reflect greater chain segmental mobility in the thin films, due to the proximity of the free surfaces, and perhaps the reduced diffusional resistance for removal of the evolving volatile compounds accompanying the rearrangement reaction.

1. Introduction

Thermally rearranged (TR) polymers are a class of highly permeable materials obtained by thermally converting a solid *ortho*-functional polyimide or polyamide to the heterocyclic poly-benzoxazole (PBO) or polybenzothiazole (PBT) at a temperature above 250 °C. Owing to this high permeability to small molecules with reasonable selectivity, thermally rearranged (TR) polymer membranes have received attention recently [1].

Most TR polymer membranes have gas separation performance surpassing the "Robeson upper bound" for separation of CO_2/CH_4, O_2/N_2, CO_2/N_2 and H_2/CO_2 [2–6]. For example, one TR polymer membrane, obtained by thermally treating the precursor polymer derived from 2,2′-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (BisAPAF) and 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) at a temperature higher than 400 °C, has been reported to have a CO_2 permeability around 2000 Barrer with a CO_2/CH_4 selectivity about 45 [1]. In addition, TR membranes seem to exhibit better resistance to plasticization by highly soluble gases, like CO_2 [1]. These initial findings have stimulated research

interest in optimizing such materials and exploring their scale-up for industrial processes.

Most of the literature on TR membrane formation and properties are based on the use of thick films (tens of microns); whereas, membranes with industrially useful productivity require film thicknesses of about 100 nm [1–3,7,8]. In our recent experiments, we noticed that TR films exhibit somewhat different gas separation properties depending on their thickness [9]. This suggested that it might be fruitful to explore the dependence of the thermal rearrangement process itself on film thickness. An *ortho*-functional polyimide synthesized from 6FDA and 3,3′-dihydroxy-4,4′-di-amino-biphenyl (HAB) was used to fabricate films with thicknesses ranging from 50 nm to 100 μm. Dynamic and isothermal thermogravimetric analyses, TGA, were used to track the rearrangement based on the fact that this chemistry involves the evolution of volatile species. In addition, changes in film thicknesses before and after thermal rearrangement were also noted.

2. Experimental

2.1. Materials and polymer synthesis procedures

The precursor polyimide was synthesized from 2,2′-bis-(3,4-dicar-boxyphenyl) hexafluoropropane dianhydride (6FDA) (purity > 99.0%, Clariant) and 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB) (> 98%) (Tokyo Chemical) and named as 6FDA–HAB. Analytical grade
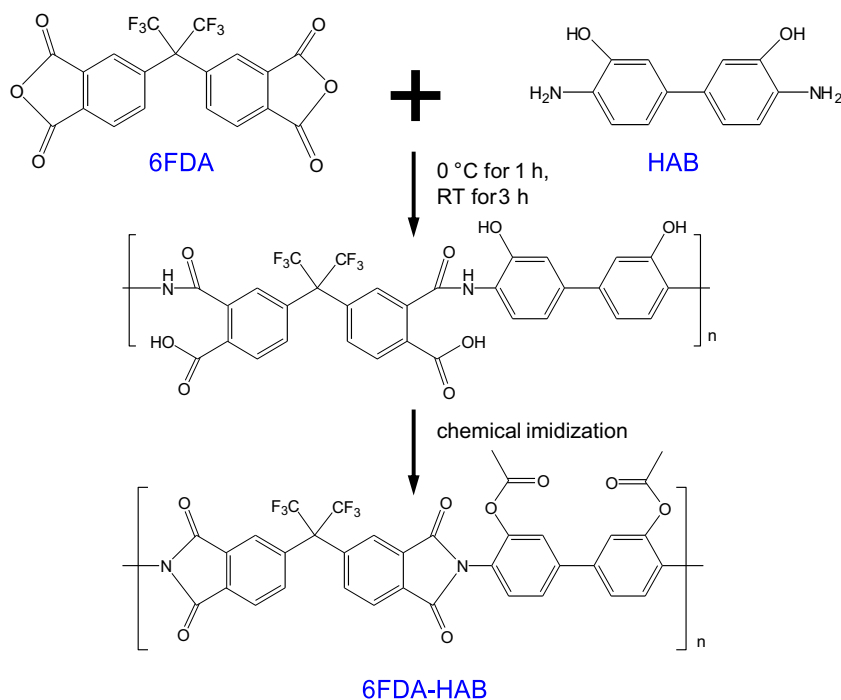
Fig. 1. Reaction scheme for 6FDA–HAB synthesis.

N-methyl-pyrrolidone (NMP) (Merck) was used as the solvent for the synthesis and was distilled under vacuum prior to use. Reagent grade cyclohexanone (purity > 99.0%, Sigma-Aldrich) was used as the casting solvent for all films.

Polymer synthesis followed the chemical imidization route using procedures described in detail elsewhere [3,10], see the reaction scheme in Fig. 1. Acetic anhydride was used as the dehydration agent for chemical imidization, and owing to the reactivity of acetic anhydride towards the hydroxyl group, acetylation of the hydroxyl group takes place at the *ortho* position during imidization.

2.2. Film preparation

The 6FDA–HAB polymer was dissolved into cyclohexanone and made into films of different thicknesses in the range of 50 nm - 100 μm by spin coating or knife casting methods.

Films with thicknesses greater than 1 μm were formed via the knife casting method. Film thickness was adjusted by varying both the solution concentration and knife clearance. The procedures for thick film casting were as follows. For example, in order to obtain a thick film of 12 μm, 0.8 g of 6FDA–HAB polymer was dissolved into 9.2 g of cyclohexanone over 3 days for complete dissolution; afterwards, the solution was filtered into a clean bottle through 1-μm PTFE filters and degassed overnight. The clean solution was cast onto an annealed glass plate with a knife clearance of 150 μm. The glass plate was then heated in a convection oven at 80 °C for 1 h to remove the solvent. The nascent film was then peeled off and dried in a vacuum oven at 170 °C overnight to remove any residual solvent.

Thin films with thicknesses in the range of 50–700 nm were prepared by spin coating the polymer solution onto a silicon wafer. The solution concentration was varied from 1 to 6 wt% polymer to control the film thickness. The polymer solution was filtered through a series of PTFE filters of 1 μm, 0.45 μm, 0.2 μm and 0.1 μm to remove dust particles and other insolubles. After degassing for 2 h, the polymer solution was spin coated at 1400 rpm for 180 s to obtain a uniform thin film. Film thickness was determined

precisely by a variable angle spectroscopic ellipsometer manufactured by J.A.Woollam Co.

The thin films used for TGA analysis were lifted from the silicon wafer by using deionized water and dried at 80 °C, followed by holding at 170 °C overnight under vacuum to remove the residual solvent. The thin films used for film thickness comparison (Section 3.1) were lifted from the wafer using deionized water and a copper-wire frame, following the procedures described elsewhere [11]. The freely standing films were dried overnight in a vacuum oven at 80 °C while still on the wire frame.

The thin 6FDA–HAB films shrank significantly during thermal rearrangement and as a result, the resultant thin films usually broke on the copper-wire frame. In order to reduce the stretching in the lateral dimension, the thin copper-wire was treated at 600 °C for 4–6 h in air prior to being used to lift the thin films. By this means, the copper-wire became more flexible and offered less resistance to deformation, but as a result the fragile thin films shrank more freely.

3. Results and discussion

3.1. Film thickness change

The thickness of thin films made by spin coating depends on the polymer concentration and the spinning conditions. The spin coating conditions were fixed at 1400 rpm for 180 s; thus, thickness was regulated by the polymer solution concentration as shown in Fig. 2.

Thermal rearrangement of 6FDA–HAB films was conducted under a nitrogen purge. The thin films were held at 200 °C for 30 min to remove moisture and residual solvent. Subsequently, the oven temperature was ramped to 370 °C and held for a certain duration. Table 1 lists the film thickness before and after thermal rearrangement. The percent increase in film thickness is calculated by

$$Thickness\ increase = \frac{\ell_t - \ell_o}{\ell_o} \times 100\% \qquad (1)$$