

Side-Chain Free Aromatic Polyimides Containing Anthracene Units Via Diels-Alder Precursors

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ABSTRACT: Side-chain free aromatic polyimides are expected to possess extraordinary mechanical properties and stability because of strong primary and secondary bonding forces. However, their low solubility makes it difficult to characterize, process, and obtain high molecular weight polymers. We have prepared highly stable thin films of side-chain free aromatic polyimides from soluble Diels-Alder (DA) precursors. Heating the films of the precursors above 215°C induced retro-DA reaction, which converted the precursors to the fully aromatic polyimides. The solid-state retro-DA reactions were monitored by attenuated total reflection Fourier transformed infrared (ATR-FTIR) and UV-

Vis spectrometry. A critical issue for utilizing precursor chemistry in polymer synthesis is that it may result in porous and/or deformed materials. In this work, profilometry and atomic force microscope (AFM) were applied to study the surface and volume change. Our results showed that smooth and pin-hole free films were obtained after the thermal treatment, while the volume decreased with a percentage close to the weight loss caused by the retro-DA reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2953–2958, 2009

Key words: polyimides; polyaromatics; thin films; morphology

INTRODUCTION

Properties of a polymer depends on its primary bonding structure that normally consists of covalent bonds, and the secondary bonding force (intermolecular interaction), which contributes to the stability of the polymer and greatly affects the mechanical and electronic properties. It is not surprising that most of the high performance polymers reported today have highly aromatic rigid rod structure.¹ Resonance energy of aromatic structure stabilizes the primary structure, while the π - π interaction strongly contributes to secondary bonding energy.² However, fully aromatic polymers normally have low solubility because of lack of flexibility and strong intermolecular interaction, which makes it difficult to characterize, process and obtain high molecular weight polymer. Introducing a flexible linker in main chain or grafting long alkyl side chains^{3–5} can significantly improve the solubility. Nonetheless, these modifications lower the primary and secondary bonding energies, thus often lowering the performance.

Precursor chemistry has been widely utilized to solve the solubility problem of highly-aromatic polymers.^{6–11} One of the precursor approaches utilized the reversible Diels-Alder (DA) reaction. In this approach,

aromatic monomers contain dienes such as anthracene and furan reacted to small dienophiles and form DA adducts. The DA adducts are polymerized to get soluble precursors. Once the precursors are processed into the desired form, thermal treatment induces retro-DA reaction that releases the small dienophile and generates the aromatic polymers in solid state. Hodge et al. reported a series paper of synthesizing highly aromatic polyamides and polyesters from precursors containing anthracene DA adduct.^{12–14} Recently, Mullen and Herwig¹⁵ and Afzali and co-workers^{16–18} have used pentacene DA adduct to solve the solubility problem of pentacene. However, a common concern of utilizing the precursor chemistry is that it may result in porous and/or deformed materials because of releasing side products in the solid-state reaction that generates the desired polymers. Although this is a critical issue for many applications, few works have been done for correlating the solid-state reaction with the morphology change.

Our group is interested in synthesizing side-chain free, highly aromatic polymers because such polymers are expected to have very strong intermolecular π - π interaction, which may result in extraordinary mechanical, thermal, electronic and optical properties. Aromatic polyimides are well known high performance polymers with high stability and good mechanical properties.¹⁹ The solubility of most reported aromatic polyimides are poor. Even for the soluble ones, high polarity and high boiling-point solvents such as Dimethyl sulfoxide (DMSO), *m*-cresol

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and H_2SO_4 are normally necessary to dissolve the polymers.²⁰ Polyamic acids, which are difficult to purify are also soluble only in high polarity solvents, often used as the precursor for preparing thin-films of polyimides²¹ Here we report the synthesis of highly-aromatic polyimides containing anthracene units via DA precursors. The surface and volume change after the solid state retro-DA reaction was studied by AFM and profilometry.

EXPRIMENTAL

Measurements

$^1\text{H-NMR}$ spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. IR spectroscopy was performed on Bruker Vertex 70 ATRFTIR. TGA were determined on a TA Instruments TGA 2050. Film thickness was determined on an Alpha Step 500 surface profiler. AFM was performed on a Dimension 3100 AFM.

Materials

2,6-Diaminoanthracene

This compound was synthesized following a literature method with modification in the purification procedure²² To a suspension of 2,6-Diaminoanthraquinone (4.36 g, 0.018 mol) in 10% sodium hydroxide solution (42 mL) was added by zinc dust (3.35 g) at room temperature. The mixture was brought heated to reflux temperature and 95% ethanol (3.5 mL) was added to prevent violent foaming. Further portions of zinc duct (2×3.35 g) were added after 30 and 60 min had elapsed. The mixture was then heated under reflux with vigorous stirring for 24 h. The solid was filtered off from the mixture and washed with hot water until the washings were clear. This crude product containing zinc residues was extracted by acetone. The acetone solution was passed through a short silica plug and the solvent was evaporated under reduced pressure. The crude product obtained was washed by acetone several times to obtain pure product. (1.5 g, 40% yield) $^1\text{H-NMR}$ (DMSO-d_6): $\delta/\text{ppm} = 7.80$ (s, 2H), 7.62 (d, 2H, $J = 8.9$), 6.91 (dd, 2H, $J = 1.22, 8.9$), 6.78 (s, 2H), 5.21 (s, br, 4H).

Diisopropyl 2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-trans-dicarboxylate (5)

Compound 5 was synthesized following a literature method with modification in the chromatography²² The crude product was purified by silica-gel chromatography using 1 : 6 ethyl acetate/dichloromethane. The yield was (85%) 0.693 g. $^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 7.06$ (d, $J = 7.8$, 1H), 6.93 (d, $J = 7.8$, 1H), 6.69 (d, $J = 2.3$, 1H), 6.54 (d, $J = 2.3$, 1H),

6.35 (dd, $J = 7.8, 2.3$, 1H), 6.38 (dd, $J = 2.3, 7.8$, 1H), 4.89 (m, 2H), 4.45 (br, 2H), 3.51 (s, br, 4H, $-\text{NH}_2$), 3.33 (m, 2H), 1.11 (m, 12H).

Diethyl 2,6-diamino-9,10-dihydro-9,10-ethanoanthracene-11,12-trans-dicarboxylate (6)

Compound 6 was synthesized via a similar procedure as the synthesis of 5 except that ethyl fumarate was used as the starting material. The yield was 2.15g, 78%. $^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 7.06$ (d, $J = 7.8$, 1H), 6.95 (d, $J = 7.8$, 1H), 6.68 (d, $J = 2.2$, 1H), 6.56 (d, $J = 2.0$, 1H), 6.38 (m, 2H), 4.47 (s, 2H, bridge), 4.06 (m, 4H), 3.51 (s, br, 4H, $-\text{NH}_2$), 3.33 (m, 2H), 1.21 (m, 6H).

Diisopropyl 2-amino-9,10-dihydro-9,10-ethanoanthracene-11,12-trans-dicarboxylate (7)

A solution of 4-aminoanthracene (2.0 g, 0.0103 mol) and isopropyl fumarate (4.72 g, 0.0206 mol) in dry chlorobenzene (5 mL) was heated under reflux for 3 days, under an atmosphere of nitrogen. The mixture was allowed to cool and most of the chlorobenzene was removed in rotary evaporator. The brown oily residue was dissolved in a small volume of chloroform. This solution was added with stirring to a large excess of hexane. The light brown precipitate formed was isolated by filtration, washed with hexane. The crude product was purified by column chromatography [silica gel, 1 : 6 ethyl acetate/dichloromethane] $^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 7.30$ (d, $J = 6.5$, 1H), 7.17 (t, $J = 7.5$, 1H), 7.0–7.1 (m, br, 2H), 6.97 (d, $J = 7.8$, 1H), 6.72 (d, $J = 2.2$, 1H), 6.39 (m, br, 1H), 4.89 (m, br, 2H), 4.57 (m, br, 2H, bridge), 3.51 (s, br, 2H, $-\text{NH}_2$), 3.36 (m, 2H), 1.19 (m, 12H).

Polymer synthesis

Precursor of polymer 1–3 was synthesized by the following procedure. The diamino DA adduct and 1 eq. of the corresponding tetracarboxylic dianhydride were dissolved in minimum amount of *m*-cresol and catalytic amount of isoquinoline (20 mol%). The reaction mixture was heated at 135°C for 12 h under N_2 , and then cooled to room temperature. Adding the solution to methanol precipitated out the crude polymer. The crude product was dissolved in minimum amount of chloroform and precipitated in hexane. The final product was then collected by filtration. Average yield was $\sim 80\%$.

Precursor of polymer 1

$^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 8.47$ (s, 2H), 7.55 (d, br, 2H), 7.46 (d, br, 2H), 7.29 (m, br, 2H), 4.91 (d, br, 2H), 4.13 (m, 4H), 3.52 (d, br, 2H), 1.27 (m, 6H).

Precursor of polymer 2

$^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 8.46$ (s, br, 2H), 7.54 (br, 2H), 7.42 (br, 2H), 7.29 (br, 2H), 5.02–4.84 (m, br, 4H), 3.45 (s, br, 2H), 1.33–1.14 (m, br, 12H).

Precursor of polymer 3

$^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 8.83$ (s, br, 4H), 7.04–7.64 (m, 6H), 4.98 (m, br, 4H), 3.57 (br, 2H), 1.22 (m, br, 12H).

Synthesis of 4

A mixture of 2.0 g (5 mmol) of **7**, 0.8 g (2 mmol) of PTCDA and 500 mg of Isoquinoline was dissolved in 55 mL of *m*-cresol. The mixture was heated to 165°C for 12–15 h, then cooled down to room temperature. The solution was added to (1/1 water/methanol) to precipitate the product. The crude product was purified by silica gel column chromatography using 7 : 3 hexane/ethyl acetate, then 17 : 3 dichloromethane/ethyl acetate). The yield was 342 mg (15%). The low yield is due to large amount of *m*-cresol used to dissolve PTCDA. $^1\text{H-NMR}$ (CDCl_3): $\delta/\text{ppm} = 8.69$ –8.41 (m, 8H), 7.50–7.07 (m, 14H), 5.01–4.72 (m, 8H), 3.53–3.43 (m, 4H), 1.27–1.13 (m, 24H).

Thin film preparation and thermal treatment

Thin films of the precursor polymers were prepared from ~ 5 weight% solutions of the polymers in 1,1,2-trichloroethane. The solutions were spin cast on glass substrates using a Laurell WS400B-6NPP spin coater. The thin films on glass substrate were heated in a vacuum oven at 240–250°C overnight or 300°C for 30 min to ensure that the retro-DA reaction was completed. The film thickness of polymer **1-3** was 0.5–1 μm and 0.4 μm for **4**.

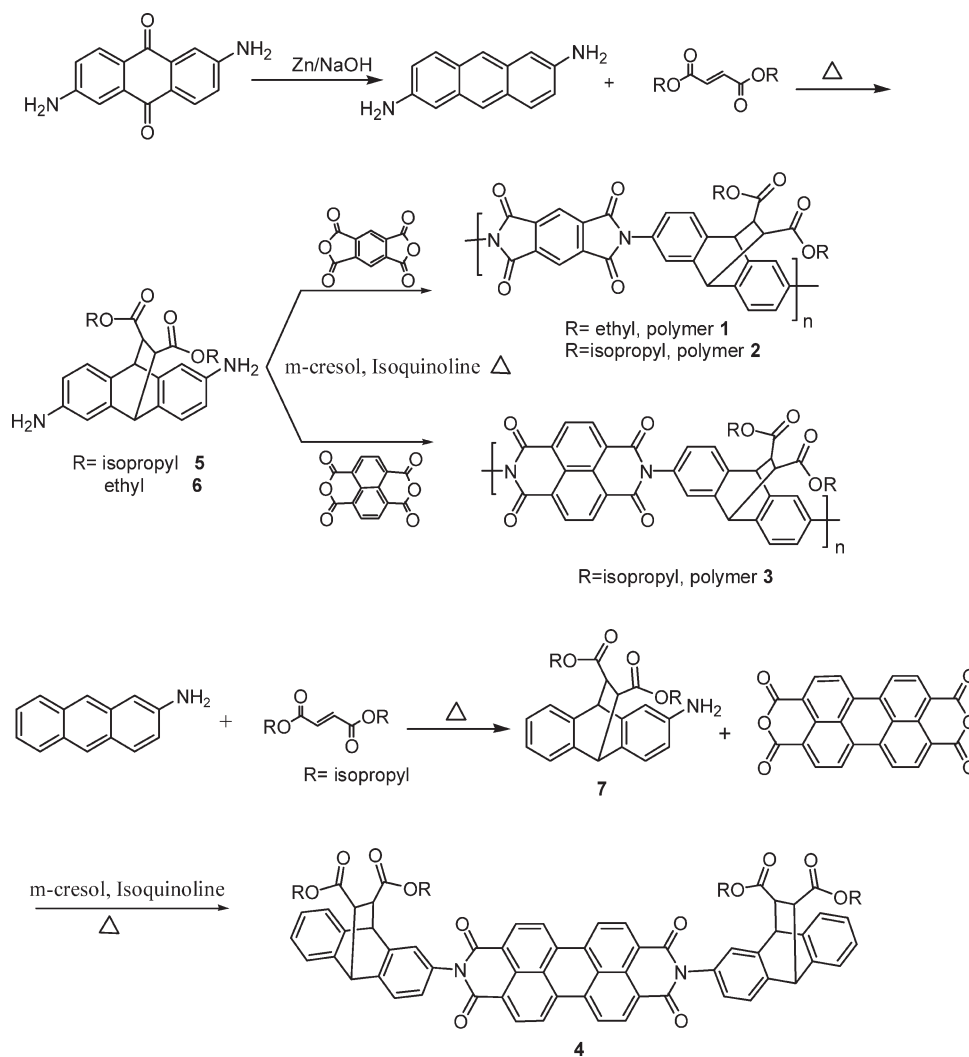
RESULTS AND DISCUSSION

The precursor Polyimides **1-3** were synthesized by condensing aromatic tetracarboxylic anhydrides with a DA adduct following the synthetic route in Scheme 1.²³ The DA adducts was synthesized from diamino anthracene²² and fumarates. Condensing the diamino DA adducts with the benzene or naphthalene tetracarboxylic dianhydrides in *m*-cresol in the presence of isoquinoline at ~ 130°C yielded the polymers. The DA adducts were fairly stable in the reaction condition. NMR showed that the integration of the peaks corresponding to the ester groups is close to the expected values. Polymerization with perylene tetracarboxylic dianhydride (PTCDA) was

unsuccessful due to the low solubility of the polymer formed. However, we were able to synthesize precursor **4** with 2 equivalence of monoamino DA adduct and 1 equivalence of PTCDA. Although the molecular weight of **4** is not high, it can be easily spin cast to thin films.

Thermal treatment is necessary to generate fully aromatic polyimides *in situ* from **1-4** via retro-DA reaction. Thermal gravity analysis (TGA) was applied to determine the required temperature for retro-DA process. Previous work has shown that retro-DA reaction of polyamides synthesized from similar DA adducts and dicarboxylic acids occurred above 200°C.¹⁴ TGA of **1-4** showed that the onset temperatures for weight loss are about same, ~ 215°C, for all the precursors. The percentages of the weight loss corresponded well with the theoretical value of fumarate dissociation. The *in situ* generated polyimides were highly stable as expected. Polyimides generated from **1-3** started decomposing above 500°C, whereas the onset decomposition temperature of **4** is about 550°C. The TGA of **4** is shown in Figure 1.

The precursors **1-4** are well soluble in chlorinated solvents such as chloroform and polar aprotic solvent such as DMSO and *N*-Methylpyrrolidone (NMP). The good solubility of the polyimides is due to the irregular zigzag conformation caused by the anthracene DA adduct and the aliphatic chains on the fumarates. Thin films of **1-4** were processed from 1,1,2-trichloroethane solutions by spin casting. Thermal treatment for retro DA reaction was conducted by heating the films either in a vacuum oven at 230°C overnight, or on a heat plate at 300°C for 30 min in air. Attenuated total reflection infrared (ATR-IR) spectroscopy is highly sensitive to vibrations of some function groups such as C=O and aliphatic C–H, and can directly analyze thin films on substrate. Therefore, ATR-IR was utilized to monitor the progress of the retro-DA reaction. Disappearance of the aliphatic C–H stretch below 3000 cm^{-1} , intensification of the aromatic C–H stretch above 3000 cm^{-1} , and decrease of the C=O stretch at ~ 1710 cm^{-1} have been observed in the IR spectra (Fig. 2), which confirmed that the retro-DA reaction was close to completion. Characteristic UV absorption of anthracene between 300 and 400 nm also appeared in after heating. (Fig. 3) The shape and intensity change of the absorption peaks between 400 and 650 nm shall be due to intramolecular interaction between thermally generated anthracene units and perylene, and increased intermolecular π - π stacking which normally broadens the line width as observed in Figure 3. In fact, after the thermal treatment, films became insoluble in all the tested organic solvents including DMSO, chloroform and chlorobenzene, which implies that



Scheme 1 Synthesis of 1–4.

the materials may find their application in thermal or photothermal patterning.

To study whether releasing dienophiles such as fumarates will result in porous surface and deformation, AFM and profilometry were applied to the thin films before and after the thermal treatment. Both analyses showed that pin-hole free, smooth surface was obtained after heating. In addition, AFM of a film of polymer 2 showed that the surface roughness decreased after thermal treatment. The root-mean-square roughness of an 80- μm area changed from 7.75 nm to 6.48 nm. (Given that no special feature was observed, the AFM spectra were provided in the supporting document.) Profilometry data showed that the thickness of the film substantially decreased after the thermal treatment. This observation may be explained by considering that, the releasing of the fumarates was accompanied by the conformation change of the polymers, which filled the space left by the fumarates. Therefore, while the process does not produce porous materials, the

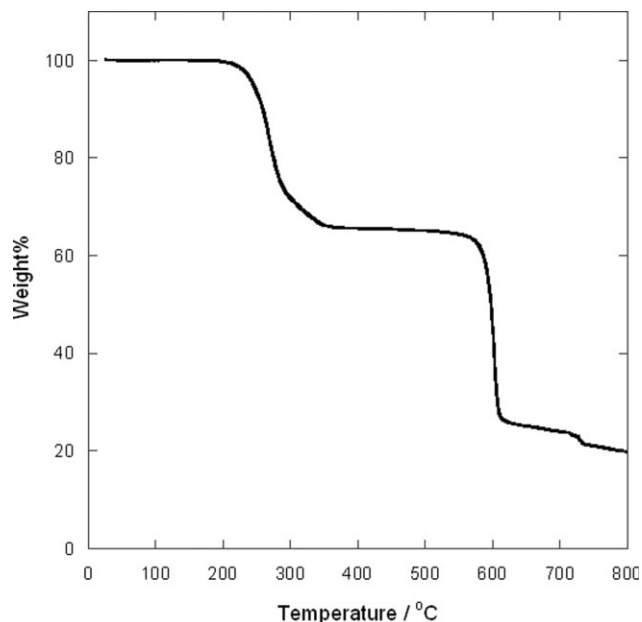


Figure 1 TGA of 4.

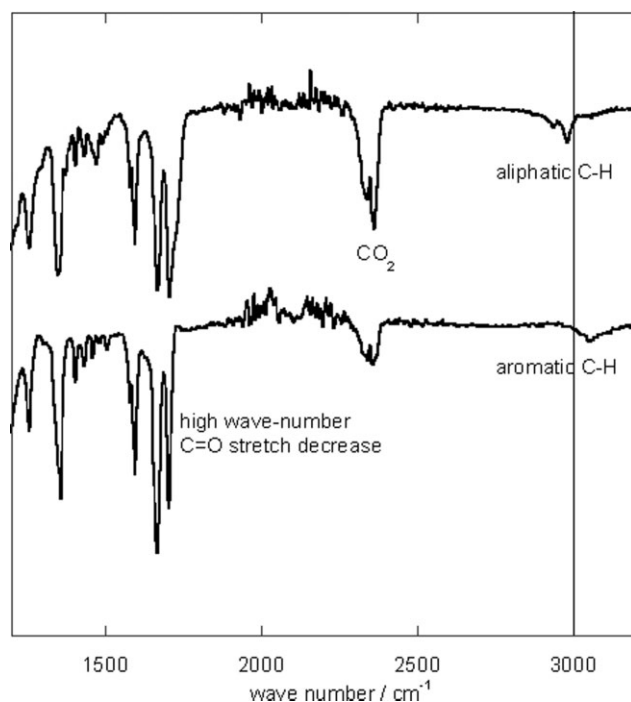


Figure 2 Infra-red spectra of 4 before (up) and after (down) thermal treatment.

volume change must be considered in the applications. The percentage of the thickness decrease for 1–4 was listed together with corresponding weight loss in Table I. Each value was obtained by averaging data from four samples. In the four-sample set

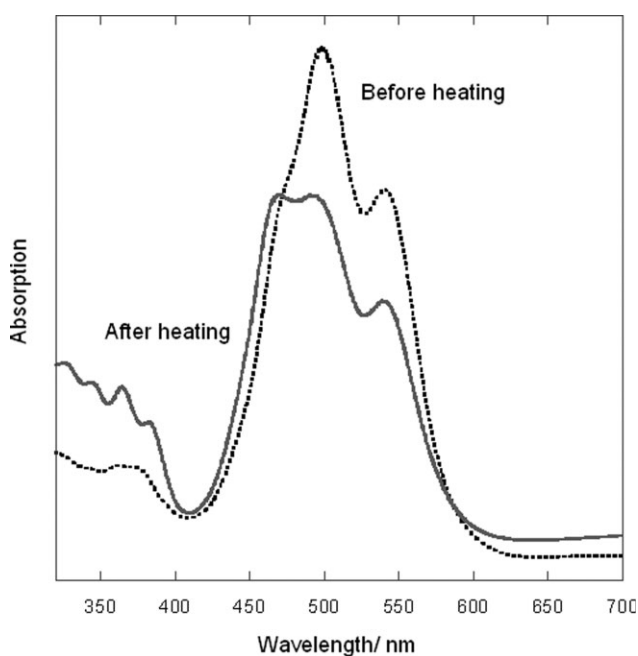


Figure 3 UV-Vis spectra of 4 before (dot line) and after (solid line) thermal treatment.

TABLE I
Thickness Decrease of 1-4 after Thermal Treatment

	1	2	3	4
Weight loss (%)	30	34	31	35
Thickness decrease (%)	32	28	26	37

of any polymer, the difference was less than 5%. As there was no substantial wrinkling observed by profilometry and AFM, the thickness decrease is approximately same as the volume decrease for the thin films. It can be seen that the volume change correlated well with the weight loss because of releasing the fumarates. In another word, the volume change of this type of materials is predictable. When the volume decrease is a major concern, small dienophiles may be used to substitute fumarates to minimize the volume change.

CONCLUSIONS

Side-chain free fully aromatic polyimides were synthesized via DA precursors. The in-film retro-DA reaction that generated the desired polymers was monitored by ATR-IR and UV-Vis spectrometry. Surface and volume change of these materials were studied by AFM and profilometry and correlated with the precursor chemistry. Results showed that smooth films were obtained and the volume decrease was predictable. When the polymer chains are aligned these side-chain free-polyimides are expected to possess extraordinary mechanic properties due to very strong intermolecular π - π interaction. However, the morphology change induced by polymer structure change is a complicated process. It is expected that the morphology of the thermally treated polymer film is frozen into a local energy minimum that is determined by the precursor structure, processing temperature, tangling of polymer chains and strong intermolecular π - π stacking. To utilize the full potential of side-chain free aromatic polyimides, processing technique such as stretching during the thermal induced retro-DA reaction may be necessary for aligning the polymer chains.

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