Design of New Polyester Architectures through Copolymerization, Crosslinking, and Diels-Alder Grafting

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Design of New Polyester Architectures through Copolymerization, Crosslinking, and Diels-Alder Grafting

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DEDICATION

I would like to dedicate this work to my dear, wondrous friends; the first people to ever treat me like I was a wonderful and beautiful human being. They are the ones who taught me that I was great just the way I was. They are the ones who set me on the path to learn how to love and accept myself. These are people I love and adore. Without them I never would have finished this piece of work. And so I dedicate it to them:

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<td>Poly(4-oxybenzoate-co-p-phenylene isophthalate-co-anthacenate)</td>
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<td>LCP</td>
<td>Liquid Crystalline Polymer</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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SUMMARY

The compound 2,6-anthracenedicarboxylic acid is used as a comonomer for the synthesis of a series of copolyesters. The copolymers are characterized and further functionalized by Diels-Alder grafting or crosslinking through the anthracenate unit. The Diels-Alder reaction is used to graft $N$-substituted maleimide on to poly(ethylene terephthalate-co-2,6-anthracenedicarboxylate), PET-$co$-A. Maleimide-capped poly(ethylene glycol) is grafted onto PET-$co$-A to improved its hydrophilicity.

2,6-Anthracenedicarboxylic acid is also incorporated into the known liquid crystalline polymer, poly(4-oxybenzoate-$co$-1,4-phenylene isophthalate) (HIQ40). The resulting copolymer, poly(4-oxybenzoate-$co$-1,4-phenylene isophthalate-$co$-2,6-phenylene anthracenate), HIQ40-$co$-A, shows LCP behavior. These HIQ40-$co$-A copolymers are grafted with maleimide end-capped monomers and polymers and crosslinked with bismaleimides through a Diels-Alder mechanism.
CHAPTER I
INTRODUCTION

Poly(ethylene terephthalate)

Since its introduction into the commercial market in 1944, poly(ethylene terephthalate) (PET) has become one of the most important polymers in the plastics industry.\(^1\) Production of thermoplastic polyester in North America in 1998 exceeded 8 billion pounds and total polyester fiber production in 1999 exceeded 35 billion pounds.\(^2\) It is a hard, stiff, strong, dimensionally stable material that absorbs very little water. It has good chemical resistance, except to alkalis. Its good processability, glass-like transparency, strength, and barrier properties are especially well suited for food and beverage containers. One of the world’s major synthetic fiber materials, it is also used in the manufacture of photographic and drafting films; magnetic, video, and computer tapes; and electrical insulators. PET is commercially prepared from terephthalic acid and ethylene glycol via a melt phase polycondensation reaction. This production method involves two stages, the first to produce bis(2-hydroxyethyl)terephthalate and small linear oligomers, and the second to remove excess ethylene glycol and drive the molecular to high values, Figure 1-1. Metal alkanoates, such as Mn(OAc)\(_2\), are added to catalyze the initial ester interchange and usually, a second catalyst, such as Sb\(_2\)O\(_3\), is added to promote the polycondensation reaction.\(^2\)

These excellent properties are also the source of some drawbacks. PET fibers are difficult to dye; tend to pill; soil easily; and have high static charge. When blended with
Figure 1-1. Synthetic steps toward the production of PET. i) cat. (if X=OMe), 190 °C, several hours. ii) cat., 290 °C, <1 torr, several hours.
cotton, the resulting fibers have lowered flame resistance. These shortcomings can be overcome by modification of PET through copolymerization or grafting.

PET copolymerization involves substituting a small amount of terephthalic acid or ethylene glycol with a diacid or diol that can survive polymerization or can be transesterified with PET. An example is the transesterification of PET with small amount of poly(ethylene glycol) in order to improve dyability and elasticity of PET fibers. Another example is the copolymerization of 1,4-phenylene bisacrylate with terephthalic acid and ethylene glycol to form poly(ethylene terephthalate-co-phenylene bisacrylate). This copolymer was designed to crosslink in the solid state upon uv irradiation. PET fibers can be made more fire resistant by copolymerizing with phosphorous containing compounds.

Grafting of PET is difficult because PET chains lack reactive groups to graft onto. Introduction of reactive groups can be achieved by treating the PET surface with free radical initiators or radiation in the presence of an unsaturated monomer or other reactant. This generally limits PET grafting to modifying only the surface layers of the treated PET material. Thus grafting is generally used to modify PET surface properties such as increasing biocompatibility and hydrophilicity, lowering static electricity, and improving adhesion.

Previous work on the synthesis of poly(ethyleneterephthalate-co-2,6-anthracenedicarboxylate) (PET-co-A) and its Diels-Alder reaction with maleimides provided a new route to PET grafting. Maleimide endcapped compounds or polymers can be grafted onto the anthracene units via Diels-Alder reactions resulting in grafted
polymer. As is shown in Chapter 2, this new technique can be used for modifying both the surface and bulk of the polymer.

**Thermotropic liquid crystalline polyesters**

Thermotropic liquid crystalline polymers (LCP) are able to form partially ordered melts. When properly processed, these can result in material with high strength, high modulus, and high thermal stability. They are often blended with other non-LC engineering polymers to afford structural composites with enhanced properties.

Aromatic homopolymers such as poly(oxybenzoate) (PHB) and poly(p-phenylene terephthalate) are so rigid that they do not melt into a liquid crystalline phase (Figure 1-2). In order to lower the melting temperature and allow for formation of a liquid crystalline phase, comonomers must be incorporated into the polymer to disrupt the strong intermolecular packing of the polymers. Several copolysters of PHB are liquid crystalline. LCP’s based on PHB include poly(oxybenzoate-co-4,4’-biphenoxy terephthalate) (Xydar™) and poly(oxybenzoate-co-ethylene terephthalate) (Rodrun™) (Figure 1-3). Copolymers containing 73 mol % hydroxybenzoic acid and 27 mol % hydroxynaphthoic acid are the basis for the Vectra® family of commercial melt processable, thermotropic, liquid crystalline copolyesters (Figure 1-3). While, poly(4-oxybenzoate-co-p-phenylene isophthalate), which is prepared from 4-hydroxybenzoic acid (H), isophthalic acid (I), and hydriquinone (Q), (HIQ) (Figure 1-3) displays a mesophases over a broad range of compositions (20 to 80 mol% H). Producing melt processable, thermotropic liquid crystalline polymers from hydroxybenzoic acid, isophthalic acid, and hydroquinone is an attractive research goal because both isophthalic
acid and hydroquinone are substantially less expensive than the alternative, hydroxynaphthoic acid.

2,6-Anthracenedicarboxylic acid is amenable to polyesterification under a variety of conditions, and possesses two modes of reactivity that allow for post-polymerization modification: photocycloaddition\textsuperscript{28} and Diels-Alder reaction.\textsuperscript{29} We sought to produce a new LCP containing 2,6-anthracenedicarboxylic acid based on HIQ40. Chapter 3 shows the synthesis, characterization, and reactivity of this new HIQ40-\textit{co}-A copolymer.
Figure 1-2. Aromatic Polyesters

poly(oxybenzoate)

poly(p-phenylene terephthalate)
Figure 1-3. Aromatic Liquid Crystalline Copolyesters.
References


CHAPTER II
SYNTHESIS AND GRAFTING OF POLY(ETHYLENE TEREPTHALATE)-CO-(ANTHRACENE-2,6-CARBOXYLATE)

Introduction

Polyesters derived from aromatic acids and aliphatic diols such as poly(ethylene terephthalate) (PET) have desirable thermomechanical properties, (i.e., \( T_g = 70 \, ^\circ\text{C}, T_m = 275 \, ^\circ\text{C} \)), that arise from the combination of rigid 1,4-phenylene units, short ethylene units, and dipolar esters. Modification of PET is desirable to enhance properties such as dye adhesion, biocompatibility, and antistatic properties. Various techniques, such as plasma discharge, chemical treatment, physical coatings, and graft copolymerization, have been applied to PET surfaces. However, these grafting reactions are of limited use due to lack of reactive sites on in the homopolymer.

Dimethyl 2,6-anthracenedicarboxylate is stable at temperatures required for polyesterification and it can be incorporated into copolymers. Previous studies indicate that poly(ethylene terephthalate-co-anthracenate) undergoes Diels-Alder additions with a variety of dienophiles. This allows for grafting of groups to PET which may have a strong influence on the physical properties of the polymer. Here PET-co-A copolymers across the composition range subjected to grafting reactions with maleimide–terminated alkyl chains to study the kinetics of the grafting reaction. These were also reacted with maleimide-terminated polyethylene glycols to modify the surface properties of the copolymers.
Experimental

Materials

All materials were obtained from Aldrich Chemical Company and used as received unless noted. PEG was obtained from Fisher Scientific. Ethylene glycol was obtained from KoSa and was used without further purification. The $O$-(2-maleimidoethyl)-$O'$-methyl-polyethyleneglycol 5000 (PEG5000M) was purchased from Fluka and used without further purification. Dimethyl 2,6-anthracene dicarboxylate, 1, and dioctyl anthracene-2,6-dicarboxylate, 2, were prepared according to previously reported methods.$^{10}$

Instrumentation

NMR spectra were obtained on Bruker AMX 500 MHz, Bruker DMX 400 MHz and Varian Gemini 300 MHz instruments. Thermal transitions of the polymers were determined using a Perkin-Elmer DSC 7 with a temperature program of three heating and cooling cycles at 10 °C/min under N$_2$. IR spectra were collected using KBr pellets, solution-cast films (TFA/CHCl$_3$) of polymers, or attenuated total reflectance (ATR) cell. Contact angle measurements on 1 μm distilled water drops were performed on a locally constructed contact angle goniometer. The data presented is the average of at least five measurements. Films were spin coated from TFA solution (0.1-0.2 g per 10 mL of TFA) onto glass slides (25 × 25 mm) on a Specialty Coating (model P-6000) spin coater (speed 2800 rpm for 120 s).
**N-Octadecylmaleamic acid, 3**

A solution of N-octadecylamine (4.952 g, 18.37 mmol) in CHCl₃ (25 mL) was added dropwise to a solution of maleic anhydride (3.248 g, 33.07 mmol) in CHCl₃ (50 mL) and the mixture was stirred for 30 min. The mixture was vacuum filtered and the solid was washed with CHCl₃ (50 mL) and hexane (50 mL) to yield 3 as a white powder (6.022 g, 89%). mp. 104-106 °C. lit. mp. 102-104 °C.¹¹ ¹H NMR (TFA-d) δ 6.89 (d, 1H, J = 12.7 Hz), 6.80 (d, 1H, J = 12.7 Hz), 3.63 (t, 2H, J = 7.4 Hz), 1.75 (q, 2H, J = 7.4 Hz), 1.2-1.5 (m, 30H), 0.85 (t, 3H, J = 6.9 Hz). IR (neat): 3245 (br), 3070 (br), 2911, 2849, 1709, 1637, 1529, 1468, 1401, 1155, 852, 718, 636 cm⁻¹.

**N-Octadecylmaleimide, 4**

A mixture of N-octadecylmaleamic acid (5.41 g, 14.7 mmol), sodium acetate (205 mg, 25 mmol) and acetic anhydride (100 mL) was heated to 100 °C for 30 min. The mixture was cooled to room temperature and poured into an ice/water slurry. The resulting solid was vacuum filtered, and purified by column chromatography (CHCl₃, silica gel) to yield 4 as a white solid (3.24 g, 60%). mp. 76-78 °C. lit. mp. 72.-73.5 °C.¹² ¹H NMR (CDCl₃) δ 6.66 (s, 2H), 3.48 (t, 2H, J= 7.3 Hz), 1.54 (m, 6H), 1.23 (m, 32H), 0.86 (t, 3H, J = 6.8 Hz). IR (neat): 2916, 2844, 1699, 1653, 837, 698 cm⁻¹.

**N-(4-Dodecylphenyl)maleamic acid, 5**

A solution of 4-dodecylaniline (5.00 g, 19.1 mmol) in CHCl₃ (30 mL) was added dropwise to a solution of maleic anhydride (2.81 g, 28.7 mmol) in CHCl₃ (30 mL) and the mixture was stirred for 30 min. The mixture was vacuum filtered, and the solid was washed with CHCl₃ to yield 5 as a white solid (5.09 g, 75%). mp. 130-135 °C. ¹H NMR
(DMSO-$d_6$) $\delta$ 7.49 (d, 2H, $J = 8.2$ Hz), 7.11 (d, 2H, $J = 8.2$ Hz) 6.45 (d, 1H, $J = 12.1$ Hz), 6.27 (d, 1H, $J = 12.1$ Hz), 2.47 (m, 2H), 1.50 (m, 2H), 1.2 (m, 18H), 0.83 (t, 3H, $J = 7.0$ Hz). IR (neat): 3305, 3215, 2961, 2912, 2849, 1726, 1628, 1545, 1500, 850 cm$^{-1}$.

$N$-(4-Dodecylphenyl)maleimide, 6

A mixture of $N$-(4-dodecylphenyl) maleamic acid (5.00 g, 13.9 mmol), sodium acetate (1.825 g, 22.2 mmol) and acetic anhydride (50 mL) was heated at 100 °C for 30 min. The reaction was cooled to room temperature and poured into an ice/water slurry. The solid was vacuum filtered to yield 6 as a white solid (4.27 g, 90%). mp. 60-65 °C. lit. mp. 67-68 °C.$^{13}$ $^1$H NMR (CDCl$_3$) $\delta$ 7.22 (q, 4H), 6.82 (s, 2H,), 2.62 (t, 2H, $J = 7.3$ Hz), 1.61 (m, 2H), 1.26 (m, 18H), 0.83 (t, 3H, $J = 6.9$ Hz). IR (neat): 3086, 2911, 2844, 1699, 1514, 1401, 1160, 831, 713, 693 cm$^{-1}$.

Diels-Alder Adduct of Dioctyl 2,6-Anthracenedicarboxylate

A mixture of Dioctyl 2,6-Anthracenedicarboxylate (9.5 mg, 1.9 $\times$ 10$^{-5}$ mol) and $N$-Octadecylmaleimide (6.8 mg, 1.9$\times$10$^{-5}$ mol) was prepared by dissolving in CHCl$_3$ (2 mL), then evaporating solvent. The solid mixture was heated at 130 °C for 30 h, resulting in formation of Diels-Alder adduct. $^1$H NMR (CDCl$_3$) $\delta$ 8.02 (d, 1H, $J = 1.2$ Hz), 7.93 (d, 1H, $J = 1.2$ Hz), 7.88 (d of d, 1H, $J = 7.7$, 1.5 Hz), 7.84 (d of d, 1H, $J = 7.7$, 1.5 Hz), 7.44 (d, 1H, $J = 7.1$ Hz), 7.35, (d, 1H, $J = 7.1$ Hz), 4.9 (multiplet, 2H), 4.27 (t, 2H, $J = 6.6$ Hz), 4.23 (t, 2H, $J = 6.6$ Hz), 3.21 (d of d, 1H, $J = 3.2$, 8.5 Hz), 3.16 (d of d, 1H, $J = 3.2$, 8.5 Hz), 3.06 (t, 2H, $J = 7.32$ Hz), 1.72 (m, 4H), 1.57 (m, 8H), 1.23 (m, 50H), 0.86 (m, 9H).
Polymer Synthesis

Dimethylterephthalate, ethylene glycol, Mn(OAc)$_2$, Sb$_2$O$_3$, and 1 were mixed in a stirred glass reactor at 190 °C under nitrogen for several hours until the distillation of methanol ceased. A single drop of 10% (w/w) in ethylene glycol was added to the reaction mixture. The reaction was heated to 290 °C while the pressure was slowly reduced to below 1 torr over the course of 1 h. The polymer was held at 290 °C for several hours, the reaction vessel was flushed with nitrogen, and cooled to room temperature to give the copolymers as yellow/green solids.

Bulk Grafting

A mixture of the copolyester containing 15 mol% of the 2,6-anthracenedicarboxylate repeat unit (PET-co-15A) (387.0 mg) and N-octadecylmaleimide (140.0 mg) (a 1.0:1.4 anthracene to maleimide molar ratio) were prepared in CHCl$_3$ containing 5% v/v trifluoroacetic acid (TFA) (10 mL), followed by removal of the solvent on a rotary evaporator. The solid residues were dried under vacuum at room temperature, overnight, and heated at 225, 200, 150, or 130 °C. The extent of reaction was determined as a function of time by $^1$H NMR spectroscopy. Excess N-octadecylmaleimide was removed by reprecipitation from chloroform solution. A blend of PET15A (72.0 mg) and 4-(dodecylphenyl)maleimide (26.2 mg) (a 1.0:1.1 anthracene to maleimide molar ratio) was similarly prepared.

Surface grafting

Films of PET, PET-co-15A and PET-co-2.5A were spin coated from TFA solution (50-70 mg in 5 mL of TFA) onto glass slides. The films were washed with water
in soxlet extractor, dried in a vacuum oven at 80 °C, and the contact angle of a 1 µL water droplet was measured. One set of films was treated with PEG5000M by evaporating 400 µL of solution (90 mg in 5 mL of CHCl₃). Another set was treated with chloroform (400 µL of CHCl₃ evaporated on films) without PEG5000M according to the same procedure. These films were heated at 160 to 180 °C for 45 min, washed in a beaker with boiling water for 1-2 h, dried, and the contact angle remeasured. The films were washed repeatedly until the water contact angle on films treated with PEG5000M remained constant between washings.

Results and Discussion

Synthesis

Dimethyl 2,6-anthracenedicarboxylate, 1, was synthesized in six steps from p-toluoyl chloride and p-xylene. A standard two-step procedure was used for the preparation of N-substituted maleimides. A solution of amine was added dropwise to a solution of maleic anhydride to afford the corresponding maleamic acid. Ring closure of the maleamic acid was performed in acetic anhydride containing a catalytic amount of sodium acetate.

Copolymers of the 2,6-anthracenedicarboxylate were prepared by catalyzed melt transesterification of dimethyl terephthalate, dimethyl 2,6-anthracenedicarboxylate, and ethylene glycol (Figure 2-1). This polymerization methods proceeds in two steps, an initial transesterification to form bis(2-hydroxyethyl) terephthalate and oligomers of PET as well as bis(2-hydroxyethyl) anthracene-2,6-dicarboxylate. Mn(OAc)₂, promotes the transesterification but also can promote the depolymerization of polyester in the second
Figure 2-1. Synthesis of Anthracene containing colpolyesters. (a) i. Mn(OAc)$_2$, Sb$_2$O$_3$, 190°C, 2 h. ii. 290°C, 0.5 torr, 2.5 h.
Poly(phosphoric acid) in ethylene glycol was added to sequester the manganese prior to raising the temperature and reducing the pressure. A second catalyst, Sb$_2$O$_3$, was used to promote the polycondensation reaction and ultimately give high molecular polymer. The polymerization reaction mixture remained fluid throughout the entire polymerization reaction. Copolyesters containing 2.5, 5, 10 and 15 mol% anthracene were polymerized.

**Polymer Characterization**

The compositions of the copolymers were determined by comparison of the integrals in the $^1$H NMR spectra for the singlets at 8.97 and 8.71 ppm (corresponding to two protons each on C-9,10 and C-1,5 of the anthracene units, respectively) to the singlet at 8.23 ppm (corresponding to the four equivalent protons of the terephthalate structural unit). For the copolymers that were soluble, and thereby amenable to study by NMR, the compositions were in accord with the monomer feed.

Small amounts of anthracene structural units in the copolymers of PET result in an increase in the glass transition temperature, $T_g$, and a decrease in melting point, $T_m$ (Figure 2-2 and 2-3). The endothermicity of the melting transition decreases upon increasing the amount of the anthracene comonomer in the polymer, and copolymers with greater than 15% of the anthracene structural unit are completely amorphous up to the temperature at which they decompose, and they do not demonstrate glass transitions or melting. Annealing these samples for 12 to 36 hours did not induce crystallization.

**Thermal Analysis of PET15A/maleimide blends**

Differential scanning calorimetry (DSC) thermogram of N-octadecylmaleimide shows a complex melting endotherm upon heating, with two peaks at 60 and 65 °C ($\Delta H$
Figure 2-2. Glass transition temperatures of poly(ethylene terephthalate)-co-(ethylene anthracene-2,6-dicarboxylate)s.
Figure 2-3. Thermograms of selected poly[(ethylene terephthalate)-co-(ethylene anthracene-2,6-dicarboxylate)]s.
= 147 J/g) and a crystallization exotherm on cooling with two peaks at 42 and 39°C ($\Delta H = -150$ J/g). A thermogram of a 1:1 mixture of N-octadecylmaleimide and dioctyl 2,6-anthracenedicarboxylate shows endotherms for the melting of both compounds followed by a broad exotherm at 114 °C with an enthalpy change corresponding to -101 kJ/mol of Diels-Alder adduct formed. The $^1$H NMR of the sample after the DSC experiment indicates formation of Diels-Alder adduct (see Exp. Sec.).

Similarly, a mixture of PET-co-15A and N-octadecyl maleimide (1:1.4) also shows an endotherm with two peaks at 60 and 67 °C ($\Delta H = 150$ J/g maleimide; 40 J/g mixture) upon first heating (Figure 2-4). The heat of enthalpy is consistent with the melting of phase-separated N-octadecylmaleimide in the mixture. This is followed by a broad exotherm with a peak at 151 °C, ($\Delta H = -49$ J/g of mixture; -92.1 kJ/mol Diels-Alder adduct), corresponding to grafting of the maleimide to the anthracene structural units in the copolymer by a Diels-Alder reaction (Figure 2-4). None of these peaks is apparent upon cooling or reheating the sample. Subsequent heating and cooling cycles show only a glass transition at 45 °C, ($\Delta C_p = 0.4$ J/g) (Figure 2-3, 2nd cycle). The glass transition of the grafted copolymer increases to 59.3 °C after removal of unreacted N-octadecylmaleimide by reprecipitation from chloroform solution.

Evidence for formation of the Diels-Alder adduct (Figure 2-5) of the copolymers was obtained by $^1$H NMR spectroscopy. For example, the peaks at $\delta$ 8.84 and 8.59 ppm for the C-1,5 and C-9,10 protons of the anthracene unit are absent from the $^1$HNMR spectrum of the product obtained upon treatment of PET-co-15% A with N-
Octadecylmaleimide. Peaks corresponding to the Diels-Alder adduct appear at δ 7.96 for the C-1,5 protons and at 4.95 ppm for the C-9,10 bridgehead protons (numbers refer to Figure 2-4. DSC of PET-co-A and N-octadecyl maleimide (1:1.4) mixture.
Figure 2-5. Grafting reaction of PET- co- A and N-octadecyl maleimide.
the numbering system for anthracene). The peaks at δ 8.05 ppm for the C-4,8 protons of the anthracene unit shift upfield to δ 7.45 ppm after the reaction. A new signal at δ 3.08 ppm in the spectrum of the Diels-Alder adduct corresponds to the hydrogen on the fused maleimide ring. Since an excess of the maleimide was used, the peaks at δ 6.66 ppm for the protons of the double bond decrease in intensity but do not completely disappear, until excess reagent is removed by reprecipitation. The triplet at δ 3.48 ppm of the CH\textsubscript{2} protons alpha to the nitrogen of the maleimide shifts upfield to δ 3.38 ppm upon grafting.

The course of the Diels-Alder reaction was followed as a function of time and temperature by heating mixtures of \textit{N}-octadecyl maleimide with PET-co-15A (1.4:1.0) were heated at 225, 200, 150, and 130 °C. The extent of the Diels-Alder reaction was monitored the decrease in intensity of the anthracene peaks at δ 8.84 and 8.59 ppm and the appearance of the new peaks at δ 7.49 and 7.41 ppm for the adduct in the \textsuperscript{1}H NMR spectrum. Plots of the conversion to Diels-Alder adduct versus time at various temperatures are presented in figure 1-6. At 200 and 225 °C, the Diels-Alder reaction goes to completion after less than 3 min. At lower temperatures the reaction takes much longer, although it does proceed below the melting point of the copolymer. Upon complete grafting of PET-co-15A with \textit{N}-octadecyl maleimide, the copolymer is rendered soluble in chloroform. Blends of PET-co-15A and \textit{N}-(4-dodecyl)phenylene maleimide show similar reactivity. While, blends of PET-co-15A and poly(ethylene glycol) (PEG5000M) endcapped with maleimide only showed less than 5% reaction after heating for 5 minutes at 200 °C. In this case, phase separation between the polyester and maleimide-substituted polyether impedes the reaction of the diene and dienophile.
Figure 2-6. Extent of grafting at different reaction temperatures.
Contact angle measurements of water droplets on maleimide grafted PET-co-15A were measured. Spin coated films of PET-co-15A grafted with N-octadecyl maleimide gave a contact angle of 83 ± 3.0° compared to 74 ± 3.0° for PET-co-15A. Thus, modification of the bulk polymer with N-octadecyl maleimide renders the material slightly more hydrophobic.

**Surface Modification**

In addition to grafting to the anthracene units throughout the bulk of the samples, we also sought to perform modification of the interfacial properties of PET by grafting to the surface of PET-co-A films. In particular, we set out to modify the hydrophilicity of PET surfaces by grafting long alkyl or oligoethylene glycol chains to the anthracene units on the surface of films of PET-co-A. We were able to monitor the surface grafting reaction by measuring the contact angle of water droplets of modified films.

Films of PET, PET-co-15A, PET-co-10A and PET-co-2.5A were spin coated on glass slides and dried under vacuum at 80 °C. Solutions of PEG5000 maleimide in chloroform were evaporated on the crystallized spin-coated films of PET-co-A. The films were heated to 165-180 °C and washed in a hot water bath to remove unreacted PEG5000-M. Whereas PET-co-A modified by the Diels-Alder reaction to incorporate flexible side chains throughout the bulk of the sample is soluble in organic solvents, these films remain insoluble, consistent with only a small amount of modification at surface. Figure 1-7 shows the contact angle of water before and after grafting. The contact angles of the control samples (not treated with PEG5000M) remained the same after the heating
Figure 2-7. Contact angle of PEG-grafted PET-co-15A.
and rinsing procedure. The contact angle of the PET homopolymer treated with PEG5000M was also unchanged after removal of physisorbed, unreacted, PEG5000 maleimide. However, PET-co-15A, PET-co-10A, and PET-co-2.5A treated with PEG5000M showed a significant decrease in the contact angle of water, indicative of a grafting reaction. PEG5000M treated PET-co-15A films showed a 22° decrease in the contact angle of water droplets to 52 ± 2°, while treated PET-co-10A and PET-co-2.5A films showed a decrease to 54 ± 2° and 56 ± 2° respectively. Thus, modification of PET-co-A films with PEG5000M is restricted to the surface by this procedure, which renders the polyester hydrophilic.

Conclusions

The formation of copolyesters containing less than 20mol % of the 2,6-anthracene dicarboxylate structural units provides materials that are tractable and soluble. Poly(ethylene terephthalate-co-anthacenate) copolymers undergo Diels-Alder grafting with N-substituted maleimides to afford side chain-substituted and branched copolymers. The rate of reaction between the anthracene units of PET-co-A and maleimides is controlled by the temperature and degree of phase separation between the components. Modification of the surface of PET-co-A films has been accomplished through the Diels-Alder reaction of maleimide endcapped PEG to anthracene dicarboxylate residues. Thus, incorporation of a small amount of the 2,6-anthracene structural unit into PET affords the opportunity to modify the polyester through chemical reactions without sacrificing many of the attractive thermal (and thermomechanical) properties of the homopolymer.
References


CHAPTER III

MODIFICATION OF POLY(4-OXYBENZOATE-co-PHENYLENE ISOPHTHALATE) WITH 2,6-ANTHRACENE DICARBOXYLATE

Introduction

Processing thermotropic liquid crystalline polymers (LCP) from the partially ordered melt provides highly oriented materials with high strength, modulus and thermal stability. Problems in the production of these include the expense of process and starting materials. As a result, LCP’s are often blended with other non-LC engineering polymers to afford structural composites with enhanced properties. This leads to problems of blending incompatibility and poor adhesion since not all polymers are compatible with TLCPs.

Polymeric liquid crystals are based on rod-like structures incorporated either into the backbone or a side chain of the polymer. Main chain LCP exhibit the technologically useful property of adopting a highly parallel arrangement of the polymer chain under relatively low shear. Polymers of this type consist of a series of short rigid rod-cyclic elements such as 1,4-phenylene or 2,6-naphthalene units. The simplest polyesters possessing such structures, poly (1,4-oxybenzoul) and poly(1,4-phenylene terephthalate), (Figure 3-1), melt at such high temperatures that any thermotropic behavior is masked by decomposition. In order to reveal the thermotropic behavior of such polymers, comonomers are introduced to reduce the melting point of such fully aromatic polyesters. One such copolymer is poly(4-oxybenzoate-co-p-phenylene isophthalate), HIQ. Poly(4-oxybenzoate-co-p-phenylene isophthalate), which is prepared from 4-hydroxybenzoic
acid (H), isophthalic acid (I), and hydriquinone (Q). (Figure 3-1) displays a mesophases over a broad range of compositions (20 to 80 mol% H).\textsuperscript{1-6} Extensive studies of structure-property relationships of HIQ copolymers appear in the literature.\textsuperscript{1-21} The copolymers containing 30 to 40 mol\% HBA (i.e., HIQ40) exhibit the lowest crystalline to nematic transitions and highest solubility of the HIQ copolyesters.\textsuperscript{2,5,7,10} The thermal transitions of HIQ40 show a strong dependence on the thermal history of the sample. The glass transition temperature in the range of 125 to 141 °C and a crystal to nematic transition appears between 300 and 375 °C.\textsuperscript{10} Unfortunately the copolymers start to decompose before a clearing temperature to the isotropic melt can appear.

Previous studies on the effect of modifying HIQ copolymers show that replacing the angular isophthalate units with symmetrical rod-like terephthalate units results in an increase in $T_{\text{C\rightarrow N}}$.\textsuperscript{1} Replacement of unsubstituted rod-like hydroquinone units with chloro-substituted hydroquinone results in a decrease in $T_{\text{C\rightarrow N}}$.\textsuperscript{1}

2,6-Anthracenedicarboxylic acid is a thermally stable monomer that has been incorporated into poly(ethylene terephthalate) under standard polymerization conditions.\textsuperscript{22} The rigid anthracene carboxylate unit increases the glass transition of PET copolymers (PET-co-A). While the monomer is stable to the harsh conditions required for the polymerization by virtue of its aromaticity, it possesses two modes of reactivity that allow for post-polymerization modification of the polymer structure. The anthracene unit undergoes addition reactions with electron deficient alkenes via Diels-Alder reactions.\textsuperscript{23}
Figure 3-1. Aromatic Liquid Crystalline Copolyesters.
The anthracene units also undergo photochemically-promoted dimerization by a [4+4] cycloaddition reaction to form crosslinks between polymer chains.\textsuperscript{24} Here we report on the incorporation of 2,6-anthracene dicarboxylate units into the HIQ40 copolymer. The anthracene unit provides functionality, which may be used to improve the physical properties of the polymers. For example the polymers could be crosslinked, whereby the liquid crystalline order is locked into place to provide a polymer with increased strength along the longitudinal axis (or increased strength along two dimensions instead of just one), mechanical properties which are stable over a much greater temperature range, increased compressive strength, and greater adhesion.

**Experimental Section**

**Materials**

All materials were purchased from Aldrich or Fischer, and used as received unless otherwise noted.

**Spectroscopy**

Nuclear magnetic resonance (NMR) analyses were performed on a 300 MHz Varian Gemini 2000 instrument, a Bruker DMX 500 MHz instrument, or a Bruker 400 MHz instrument using TFA/CDCl\textsubscript{3} (1:5 v/v) as solvent. Infrared (IR) characterization was performed using a Nicolet 520 FTIR spectrophotometer. UV-VIS characterization was performed using a Shimadzu UV-160 spectrophotometer.
Thermal Analysis

Differential scanning calorimetry thermograms were obtained using a Perkin-Elmer Series 7 Differential Scanning Calorimeter equipped with an intracooler under a nitrogen atmosphere. Samples were placed in aluminum pans. The power and temperature axis were calibrated against an indium standard. The temperature program provided heating and cooling cycles at 20 °C/min between 50 °C and 400 °C, unless otherwise stated.

Spin Coated Film Preparation

Films were spin coated from 4 wt% solutions of polymer in trifluoroacetic acid (TFA)/methylene chloride (CH₂Cl₂) (3:7 v/v) onto glass slides. Films were spin coated using a Specialty Coating Inc. P6000 Spin Coater at a speed of 1500 rpm.

Polymer Film Irradiation

Photoirradiation was performed using a Rayonet photochemical reactor equipped with medium pressure Hg bulbs producing a maximum intensity at 300 nm or at 350 nm.

Poly(4-oxybenzoate-co-1,4-phenylene isophthalate) (HIQ40)

HIQ40 was prepared from 4-acetoxybenzoic acid (12.0148 g, 0.6670 mol), isophthalic acid (8.3082 g, 0.5001 mol), and diacetoxyhydroquinone (9.7142 g, 0.5002 mol) in the absence of catalyst according to a modified literature procedure (Table 3-1).⁴,⁷,⁸ Monomers were charged into a glass polymerization reactor equipped with a steel overhead mechanical stirrer and a gas inlet. This was purged with nitrogen for an hour, and placed in an oil bath heated at 300 °C. The reaction mixture was heated with stirring
for 30-45 min, the pressure was decreased to 0.05 mmHg, and heating was continued. The polymer was removed from the reactor, and dissolved in TFA/CH\textsubscript{2}Cl\textsubscript{2} (500 mL, 3:7 v/v). The solution was filtered and the polymer reprecipitated by addition of MeOH (1.5 L). The polymer was dried between at 120-140 °C under reduced pressure for 2 d. Solid state polymerization was performed by heating the polymers to 260 and 290 °C at 0.05 mmHg for 4h.

\textsuperscript{1}HNMR (10 % TFA-\textit{d} in CDCl\textsubscript{3}) δ 9.14-9.07 (m, 1H, \textit{I}-H\textsubscript{2}), 8.47-8.44 (m, 2H, benzoate H\textsubscript{2}), 8.85-8.50 (m, 2H \textit{I}-H\textsubscript{4}, endgroup), 8.44-8.28 (m, 2H, \textit{H}-H\textsubscript{2}, end group), 7.77-7.71 (m, 1H, \textit{I}-H\textsubscript{5}, endgroup), 7.55-7.42 (m, 2H, \textit{H}-H\textsubscript{3}), 7.42-7.29 (m, \textit{Q}), 7.19-6.96 (m, \textit{Q}, endgroup) ppm. \textsuperscript{13}CNMR (TFA-\textit{d}/CDCl\textsubscript{3}) δ 167.4 (s, C=O, \textit{I}-Q diad, see discussion), 167.0 (s, C=O \textit{I}-H diad), 166.7 (s, C=O H-Q diad), 166.2 (s, C=O, H-H diad), 155.8-155.2 (m, \textit{H}-C\textsubscript{4}), 148.9-148.4 (m, \textit{Q}-C\textsubscript{1,4}), 132.8 (d, \textit{H}-C\textsubscript{2,6}), 136.4 (s, \textit{I}-C\textsubscript{4,6}), 132.6 (s, \textit{I}-C\textsubscript{2}), 130.0 (s, \textit{I}-C\textsubscript{5}), 129.8-129.1 (m, \textit{I}-C\textsubscript{1,3}), 127.0-126.5 (m, \textit{H}-C\textsubscript{1}), 123.2 (s, \textit{Q}-C), 122.5 (s, \textit{H}-C\textsubscript{3,5}).

Poly(4-oxybenzoate-co-1,4-phenylene isophthalate-co-2,6-phenylene anthracenate).

Copolyesters were prepared from 4-acetoxybenzoic acid, isophthalic acid, 2,6-anthracenedicarboxylic acid, and diacetoxyhydroquinone in the absence of catalysts according to method described above for polymerization of HIQ40 (Table\textsubscript{3-1}). Representative data with assignments of peaks to individual structural units are provided.

\textsuperscript{1}HNMR (TFA-\textit{d}/CDCl\textsubscript{3}) δ 9.20 (s, \textit{A}-H\textsubscript{1,5}), 9.14-9.07 (m, 1H, \textit{I}-H\textsubscript{2}), 9.00-8.97 (m, 1H, endgroup, \textit{I}-H\textsubscript{2}), 8.81-8.85 (m, \textit{A}-H\textsubscript{9,10}), 8.85-8.75 (m, \textit{A}-H\textsubscript{9,10} end group), 8.64-8.55
Table 3-1. Loading and Yield ratios for Synthesis of HIQ-co-A

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*a* polym time  
*b* ssp time
(m, 2H, I-H_1), 8.55-8.50 (m, 2H, I-H_4, endgroup), 8.47-8.44 (m, 2H, H-H_2), 8.44-8.28 (m, 2H, H-H_2, end group), 8.20-8.35 (m, A-H_3,4,7,8) 7.88-7.77 (m, 1H, I-H_5), 7.77-7.71 (m, 1H, I-H_5, endgroup), 7.55-7.42 (m, 2H, H-H_3), 7.42-7.29 (m, Q), 7.19-6.96 (m, Q, endgroup) ppm. ^13^CNMR (TFA-d/CDCl_3) δ 167.4 (s, C=O, I-Q), 167.0 (s, C=O I-H), 166.7 (s, C=O H-Q), 166.2 (s, C=O H-H), 155.8-155.2 (m, H-ether ipso C), 148.9-148.4 (m, Q ether ipso C), 132.8 (d, H-C ortho to C=O), 136.4 (s, I-C ortho to C=O), 130.0 s, I-C meta to C=O), 129.8-129.1 (m, I-C ipso to C=O), 127.0-126.5 (m, H-C ipso to C=O), 123.2 (s, Q) 122.5 (s, H-ortho ether C).

Results and Discussion

Polymer Synthesis

Copolysteres containing 2,6-anthacene dicarboxylate together with 40 mol% 4-acetoxybenzoic acid, isophthalic acid, and 30 mol% diacetoxyhydroquinone (HIQ40-A) were prepared by an uncatalyzed polymerization according to a modified literature procedure (Figure 3-2). A mixture of monomers was stirred at 300 °C for 45 minutes to give a homogenous melt. During this initial and subsequent heating, a small amount of hydroquinone sublimes from the reactor. A small excess of hydroquinone was added in order to make up for this loss. The pressure was then reduced to remove acetic acid from the mixture. After 15 min under vacuum, all of the copolymers solidified in the reactor. The solid was removed from reactor, and subjected solid-state polymerization at 260-290
Figure 3-2. Synthesis of poly(4-oxybenzoate-\textit{co}-\textit{p}-phenylene isophthalate-\textit{co}-2.6-phenylene anthracenate) (HIQ40-A).
°C under vacuum. The polymers were reprecipitated from TFA/CH$_2$Cl$_2$/MeOH prior to analysis.

Structural Determination

The ratio of the four structural units in HIQ-co-A copolyesters was determined by $^1$H NMR spectroscopy. This showed that the monomers were incorporated in a ratio consistent with the loading ratios (see Experimental Section for peak assignments). All of the peaks appear as multiplets, since the chemical shift of each proton is sensitive to the sequences of units in the backbone. For example, the peak for the proton on C$_2$ of the isophthalate gives three singlets at $\delta$ 9.1 ppm in the $^1$H NMR spectrum arising from the three tryads that can form with an isophthalate unit in the middle: $Q$-$I$-$Q$, $H$-$I$-$H$, and $H$-$I$-$Q$.

Representative $^1$H NMR spectra of HIQ40-2.5A before and after solid-state polymerization are shown in Figure 3-3. After solid-state polymerization, the molar ratio of the $H$, $I$, $Q$, and $A$ units are 41.1 : 26.7 : 29.7 : 2.5, in close accord with the ratio of monomers used. The spectra clearly show the presence of isophthalate and quinone end groups. Whereas the peak at $\delta$ 9.14-9.07 ppm is assigned to the proton on C$_5$ of these isophthalate units in the main chain, a small peak at 8.95 corresponds to the C$_5$ proton in an isophthalic acid unit located at the chain end. Solid-state polymerization increases the ratio of main chain to end chain isophthalate units from 10:1 to 27:1. Similarly, peaks at $\delta$ 7.42-7.29 ppm and at 7.15 and 7.05 ppm correspond to protons on the quinone in the main chain and termini, respectively. In this case, solid-state polymerization increases the main chain to end group ratio from 20:1 to 40:1. The peaks for oxybenzoate and
Figure 3-3. $^1$H NMR spectrum of HIQ40-2.5A after solid-state polymerization.
Figure 3-4. Carbonyl region of the $^{13}$C NMR spectrum of HIQ40.
anthracenate end groups are too close to those of the main chain to calculate the end
groups ratio to main chain. Assuming equal reactivity of the functional groups of each
monomer and their incorporation as end groups in the same ratio as the monomer feed.
This corresponds to an approximate molecular weight for the copolymer of 9000.
The $^1$H NMR spectra do not allow us to determine the population of each possible diad in
the polymer. However, the carbonyl region of the $^{13}$C NMR spectrum$^{11}$ of HIQ40, Figure
3-4, has a peak for each of the four possible diads: $I$-$Q$, $I$-$H$, $H$-$H$, and $H$-$Q$. The ratio of
integrals of each of these signals is in agreement with the ratio predicted for a random
distribution of dyads: 1.6 $I$-$Q$:1.4 $I$-$H$:1.0 $H$-$H$:1.3 $H$-$Q$. The $^{13}$C NMR spectrum of the
soluble HIQ-$co$-$A$ copolyesters did not show anthracenate carbonyl peak because the
concentration of of anthracenate was too small for detection.

Dilute solution viscosities of copolymers were measured in a 30/70 (v/v) mixture
of trifluoroacetic acid and methylene chloride at 22 °C in an Ubbelhode viscometer.
Table 3-2 shows the intrinsic viscosities calculated from the y-intercept of plots of $\xi_{reduced}$
and $\xi_{inherent}$ vs. concentration. The value of intrinsic viscosity for HIQ40 is consistent
with those in the literature for polymers prepared under similar conditions.$^{4,7}$ Within the
HIQ copolymer series there is a strong dependence of intrinsic viscosity on the amount of
oxybenzoate (H) incorporated: the intrinsic viscosity increases with the amount of
oxybenzoate unit incorporated. Mark-Houwink parameters for HIQ polymers are not
available from the literature and molecular weights are generally not determined. For our
Table 3.2 Intrinsic Viscosity Of HIQ40 Copolyesters (dL/g) at 22 °C

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<td>0.61 ± 0.06</td>
</tr>
</tbody>
</table>

$^a$y-intercept of $\zeta_{\text{reduced}}$ and $\zeta_{\text{inherent}}$ vs. concentration plot

$^b$average of single point intrinsic viscosity
anthracenate-containing copolymers, all were prepared under similar conditions, the intrinsic viscosity decreases as the amount of anthracenate units increase (replacing isophthalate). The correlation between copolymer composition (IA ratio) clearly has an influence on the IV of these materials, as well as the molecular weight.

**Thermal Characterization**

The thermal behavior of HIQ40 is highly dependent on its thermal history. On first heating, reprecipitated HIQ40 shows a \( T_g \) of 168 °C (\( \Delta C_p = 0.27 \text{ J/g} \cdot \text{°C} \)) and a crystalline-to-nematic transition endotherm, \( T_{C \to N} \), at 335 °C (\( \Delta H = 6.4 \text{ J/g} \)). The \( T_g \) of 168 °C is unusually high relative to previous reports of a \( T_g \) between 120 and 140 °C for non-reprecipitated material.4-7 Upon cooling from the nematic and reheating, the \( T_g \) is lowered to 127 °C (\( \Delta C_p = 0.23 \text{ J/g} \cdot \text{°C} \)) and \( T_{C \to N} \) lowered to 313 °C (\( \Delta H = 3.8 \text{ J/g} \)). These transitions are reproduced upon subsequent thermal cycles. This is consistent with previously reported thermal behavior of HIQ copolymers.4-7

Table 3-3 shows a summary of thermal transitions for anthracene-containing copolyesters obtained upon first heating (reprecipitated) and second heating (after slow cooling from nematic). As in the case of HIQ40, when the copolymers are either quenched or cooled slow (20°C/min) from the nematic phase, they show a higher \( T_{C \to N} \) and \( \Delta H_{C \to N} \) on 2nd heating than in the 1st heating cycle. On the other hand, upon cooling samples after they have been annealed at 290 °C for 2 h they display a 20-40 °C increase in melting points (Table 3-3). Thus it appears that the thermal behavior has a strong dependence on the history of the sample. Once the crystalline phase melts, the resulting nematic phase
Table 3.3  DSC Thermal Transitions of First and Second Heating Cycles

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;st&lt;/sup&gt; heating</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; heating after quench</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; heating after slow cool</th>
<th>Annealing at 290 °C for 2h, on 2&lt;sup&gt;nd&lt;/sup&gt; cooling&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$&lt;sup&gt;a&lt;/sup&gt; (Δ$C_p$)</td>
<td>$T_m$&lt;sup&gt;a&lt;/sup&gt; (Δ$H_m$)</td>
<td>$T_g$&lt;sup&gt;a&lt;/sup&gt; (Δ$C_p$)</td>
<td>$T_m$&lt;sup&gt;a&lt;/sup&gt; (Δ$H_m$)</td>
</tr>
<tr>
<td>HIQ40</td>
<td>168 (0.27)</td>
<td>335 (6.4)</td>
<td>131 (0.23)</td>
<td>313 (4.0)</td>
</tr>
<tr>
<td>HIQ40-1.2A</td>
<td>148 (0.24)</td>
<td>325 (12.1)</td>
<td>131 (0.23)</td>
<td>313 (5.3)</td>
</tr>
<tr>
<td>HIQ40-2.5A</td>
<td>120 (0.12)</td>
<td>314 (5.1)</td>
<td>119 (0.16)</td>
<td>289 (5.6)</td>
</tr>
<tr>
<td>HIQ40-5A</td>
<td>118 (0.16)</td>
<td>325 (6.5)</td>
<td>122 (0.16)</td>
<td>302 (4.0)</td>
</tr>
<tr>
<td>HIQ40-10A</td>
<td>117 (0.18)</td>
<td>275 (3.6)</td>
<td>117 (0.18)</td>
<td>257 (1.0)</td>
</tr>
<tr>
<td>HIQ40-20A</td>
<td>107 (0.16)</td>
<td>270 (1.1)</td>
<td>117 (0.11)</td>
<td>270 (1.1)</td>
</tr>
</tbody>
</table>

<sup>a</sup> °C  
<sup>b</sup> J/g °C  
<sup>c</sup> J/g  
<sup>d</sup> HIQ40-10A was annealed at 250 °C
recrystallizes only slowly upon cooling. The morphology of the new crystals formed depends on the cooling rate and annealing temperature.

Figure 3-5 shows a plot of $T_{CN}$ and $T_g$ as a function of mole % anthracenenate. Overall, as the amount of anthracene increases both $T_{CN}$ and $T_g$ thermal transitions decrease. A similar trend is seen for the melting transitions of PET-co-A copolymers. The anthracenate unit acts as an impurity that partially disrupts crystallization, thereby lowering $T_{CN}$.

Attempts at annealing copolymer samples at 380 °C for 2 h, above $T_{CN}$, annealed, showed no $T_{CN}$ subsequent thermal cycles and completely insoluble material.

Samples from each of the polymers were observed between crossed polarizers in an optical microscope while heating up to 380 °C. Before heating, the samples were amorphous, showed no birefringence. However, once these are completely melted, a flowing nematic texture is seen. Figure 3-6 shows this for plain HIQ40 and HIQ40-co-5A. The temperature at which this nematic texture is seen is dependent on the copolymer composition. As the mole % anthracene increases, the lower the onset temperature. Each of the as-polymerized HIQ40-co-A samples showed the same birefringence only after they started to melt.

**Photocrosslinking**

Anthracene undergoes rapid [4+4] face-to-face dimerization through the 9- and 10-positions upon irradiation with visible light. Irradiation of poly(ethylene 2,6-anthracene-
Figure 3-5. Thermal transitions as a function of anthracene content for HIQ40-co-A.
Figure 3-6. (a) HIQ40-co-5A at 334 °C (b) HIQ40 at 356 °C (200× magnification).
co-terephthalate), PET-co-A, affords a polymer that gels in trifluoroacetic acid but which does not dissolve, suggesting the formation of a crosslinked material. Previous studies with PET-co-A suggest that even at a low molar concentration (1% anthracene units), these polymers undergo photocrosslinking upon irradiation. With this in mind, we studied the photocrosslinking reaction of irradiated HIQ40-co-A spin-coated films by UV spectroscopy. The UV spectrum of HIQ40-co-10A shows the anthracene absorption between 400 and 500 nm has a $\varepsilon_{\text{max}}$ at 430 nm (Figure 3-7). Upon irradiation with UV light with a wavelength at 300 nm or 350 nm, the absorption at 430 nm decreases in intensity, corresponding to consumption of the anthracene units. Plots of the change of absorbance at 430 nm as a function of irradiation time are shown in Figures 3-8. Irradiation at 300 nm of HIQ40 (which contains no anthracene) results in an increase at 430 nm (Figure 3-8a). This process counters the effect of the consumption of anthracene upon irradiation of the copolymer. Irradiation at 350 nm does not cause this yellowing (Figure 3-8b). As the concentration of anthracene increases, the disappearance rate also increases.

Even though UV-Vis spectroscopy shows disappearance of anthracene, thermal analysis of irradiated films shows no evidence of crosslinking. Thermograms of HIQ40-co-A films before and after irradiation show similar transitions that are reproduced upon subsequent thermal cycles. Upon irradiation, HIQ40-co-A films still remain soluble. Solution viscosity measurements show irradiated films have the same intrinsic viscosities as solutions of non-irradiated polymer. Thus evidence shows that no crosslinking is taking place.
Figure 3-7. UV Spectra of HIQ40-10A film.
Figure 3-8. Disappearance of anthracenate unit in HIQ40-A films, irradiated at (a) 300 nm, and (b) 350 nm as a function of time.
Fries rearrangement has been shown to occur in aromatic polyesters upon UV irradiation. For example, the photo yellowing of aromatic polyesters is attributed to formation of $o$-hydroxybenzophenone though a Fries rearrangement. The resulting $o$-hydroxybenzophenone then acts as an internal UV stabilizer that blocks UV irradiation. This explains why consumption of anthracene in HIQ40-$co$-A is much slower than photocrosslinking of PET-$co$-A polymers, which do not undergo facile Fries rearrangements.

**Diels-Alder Crosslinking**

Since we were unable to show photocrosslinking of HIQ40-$co$-A, we explored the possibility of thermally crosslinking by a Diels-Alder reaction between the anthracene ring and a maleimide. First we probed the reactivity of the HIQ40-$co$-10A with maleimide by heating blends of $N$-octadecyl maleimide with HIQ40-$co$-A at 210 and 290 °C. Differential scanning calorimetry (DSC) of the $N$-octadecyl maleimide/HIQ40-$co$-10A blend shows no endotherm for the melting of the $N$-octadecyl maleimide as was seen for the PET-$co$-A blends. However, it does show an exotherm ($\Delta H = -116 \text{ J/g}$) over the range of 150-300 °C, consistent for the Diels-Alder reaction. Subsequent heating and cooling cycles show no thermal transitions, not even a $T_g$.

The extent of the grafting reaction was followed as a function of time by $^1H$ NMR spectroscopy (Figure 3-9, 10). The decrease in intensity of the anthracene $H_{9,10}$ peak at $\delta$ 8.78, and the appearance of the Diels-Alder adduct peaks at $\delta$ 5.12 (bridgehead H) and 3.22 (maleimide H) ppm corresponds to the cycloaddition reaction. At 210 °C, the Diels-Alder reaction proceeds to an equilibrium of 50% conversion after 15 min. At 290 °C, the grafting reaction goes to 80% conversion after the 2 min, Figure 3-10, and during the
first 10 min the Diels-Alder reaction proceeds to 90% conversion. After 10 minutes, the
equilibrium of the reaction shifts back toward the product (via retro Diels-Alder
mechanism), and the relative amount of anthracene observed by $^1$H NMR increases.
During the reaction, the maleimide undergoes both cycloaddition and is lost to
decomposition side reactions. After successfully grafting HIQ40-co-A with maleimides,
we wanted to prove we could also thermally crosslink these copolymers. Blends of
HIQ40-co-5A and hexamethylene bismaleimide were prepared and heated at 220°C for
10 min, under N$_2$ atmosphere. All of the blends were rendered insoluble upon heating.
The thermograms of the resulting copolymers showed no thermal transitions, giving
evidence of a crosslinked polymer network network.

**Conclusion**

HIQ40, known thermotropic liquid crystalline polyester, was synthesized and
modified by addition of 2,6-anthracenedicarboxylic acid as a co-monomer. The resulting
HIQ40-co-A copolymers showed a flowing nematic phase upon melting.

Although the HIQ40-co-A is not amenable to photocrosslinking, we have shown
that we can still modify these copolymers thermally by a Diels-Alder mechanism. By
keeping reaction times low and using an excess of maleimide, we can produce new
polymer architectures by grafting HIQ40-co-A with designer maleimides. We can also
thermally crosslink HIQ40-co-A using a bismaleimide as crosslinking agent.
Figure 3-9. Plot of Conversion of anthracene dicarboxylate units in HIQ40-co-5A to the Diels-Alder adduct upon thermal reaction with \(N\)-octadecyl maleimide at 210 °C.
Figure 3-10. Plot of Conversion of anthracene dicarboxylate units in HIQ40-co-5A to the Diels-Alder adduct upon thermal reaction with N-octadecyl maleimide at 290 °C
References


CHAPTER IV
SUMMARY AND FUTURE OUTLOOK

Grafting of Poly(ethylene terephthalate-co-2,6-anthracenedicarboxylate)

Diels-Alder reaction has been used to graft small molecules and oligomers endcapped with maleimide as dienophiles on to poly(ethylene terephthalate-co-2,6-
anthracenedicarboxylate), PET-co-A. Maleimide-capped poly(ethylene glycol) has been grafted onto PET-co-A and improved its hydrophilicity. Fibers spun out of this material maybe more “cotton like” and easier to dye. Implants made from this material may minimize protein surface interactions.

Fluorinated polymers are another type of material that maybe desirable to graft onto PET. Polymers, such as poly(olefins), that normally phase separate when blended with PET can be modified with dienophiles to provide adhesion through Diels-Alder reaction. Dyes for PET can be capped with dienophiles and covalently bonded to the main chain. Antibacterial PET-co-A fibers maybe produced. This technique can be applied to graft a myriad of compounds and polymers on to PET-co-A.
Poly(4-oxybenzoate-co-1,4-phenylene isophthalate-co-2,6-phenylene anthracenate)

2,6-Anthracenedicarboxylic acid has been incorporated into the known liquid crystalline polymer, LCP, poly(4-oxybenzoate-co-1,4-phenylene isophthalate), HIQ40. The resulting copolymer, poly(4-oxybenzoate-co-1,4-phenylene isophthalate-co-2,6-phenylene anthracenate), HIQ40-co-A, shows LCP behavior. These HIQ40-co-A copolymers can be grafted with maleimide end-capped monomers and polymers or crosslinked with bismaleimides through a Diels-Alder mechanism. The HIQ40-co-A can be grafted onto PET-co-A via a bismaleimide, providing a method for an LCP to be grafted onto PET.

The 2,6-Anthracenedicarboxylic acid can also be incorporated into other liquid crystalline polymers such as Vectra® or Rodrun.™ Then used to crosslink the material giving it strength in three dimensions. Also it can be used to adhere onto other polymers such as PET.
APPENDIX

SPECTRA