Chapter 17

2,6-ANTHRACENEDICARBOXYLATE-CONTAINING POLYESTERS AND COPOLYESTERS

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1. INTRODUCTION

Polyesters prepared from aromatic acids and aliphatic diols, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), are widely used in film, fiber, and packaging applications (1,2). The development of monomer-grade 2,6-naphthalenedicarboxylic acid has led to the introduction of poly(ethylene 2,6-naphthalate), PEN, which produces stronger fibers and films, retains the optical clarity of PET, and can be formed into food and beverage containers with superior gas barrier properties (1).

The desirable thermomechanical properties of PET ($T_g=78$ °C; $T_m=256$ °C) arise from the combination of rigid 1,4-phenylene units, short ethylene units, and dipolar esters. The additional flexibility of the 1,4-butanediyl unit of PBT allows for faster crystallization and imparts a lower glass transition temperature ($T_g=40$ °C) and a lower melting point ($T_m=230$ °C). PBT also has lower modulus and tensile strength than PET, and is often reinforced with fibers or fillers. On the other hand, the rigidity of the naphthalene units of PEN imparts a higher glass transition temperature (123 °C) that facilitates its use for food packaging applications that require hot-fill and heat sterilization. Current impediments to the more widespread use of PEN...
include the high cost of 2,6-naphthalenedicarboxylic acid and the high melt viscosity of the polymer.

Small amounts of comonomers (e.g., isophthalic acid, diethylene glycol, 1,4-cyclohexane dimethanol) are added to PET, PBT, and PEN to improve their physical properties. However, other poly(alkylene arendicarboxylate) homopolymers have not been commercialized. The vast choice of flexible and rigid structural units available for incorporation in polyesters has led us to investigate new copolymers prepared from other aromatic diacids, in particular 2,6-anthracenedicarboxylic acid. As a homolog of terephthalic and naphthoic acids, we expected the anthracenedicarboxylic acid unit to provide further enhancement of the physical properties of polyesters. In addition, while the anthracenedicarboxylic acid is aromatic, and therefore stable to the harsh conditions required for polyesterification, we also hoped to exploit the reactivity of the anthracene unit to chemically modify these new polymers and copolymers. Our work has been extended to a number of other fused arenes (3-7).

Previous reports of poly(alkylene 2,6-anthracenedicarboxylate)s (PxA) have been limited to characterization of the polymer prepared by condensation of dimethyl 2,6-anthracenedicarboxylate with 1,6-hexanediol (8), and solution phase polymerization of ethylene glycol and a Diels-Alder adduct of anthracenedicarboxylate followed by heating to effect the retro Diels-Alder reaction to give poly(ethylene 2,6-anthracenedicarboxylate), P2A (9). In this chapter we provide an overview of our work to incorporate 2,6-anthracenedicarboxylate into homopolymers and copolymers, how this unit effects the thermal properties of the polymers, and how it presents new opportunities to modify polymers by addition reactions.

2. MONOMER SYNTHESIS AND POLYMERIZATION

2.1 Monomer Synthesis

Our synthesis of dimethyl 2,6-anthracenedicarboxylate starts with the AlCl₃-catalyzed Friedel-Crafts acylation of p-xylene with 4-methylbenzoyl chloride to give 2,5,4′-trimethylbenzophenone, Figure 1 (10). Heating the neat product to reflux results in ring closure by the Elbs reaction to give a mixture of 2,6-dimethylanthracene and 2,6-dimethylanthrone. Both components of the mixture obtained from this cyclization undergo oxidation upon treatment with chromium trioxide to give a single product: 9,10-anthraquinone-2,6-dicarboxylic acid. The anthraquinone is reduced to 2,6-anthracene-dicarboxylic acid upon treatment with zinc metal in aqueous ammonium hydroxide. Our initial attempts to perform this reduction made use of a catalytic amount of copper(II) sulfate. However these reactions led