Photochemical Cross-Linking of Poly(ethylene terephthalate-*co*-2,6-anthracenedicarboxylate)

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ABSTRACT: Poly(ethylene terephthalate) copolymers containing 2,6-anthracenedicarboxylate structural units are chain extended and cross-linked by irradiation at 350 nm. The cross-linked materials were characterized by NMR, UV−vis, DSC, and dilute solution viscometry. The cross-linking is attributed to face-to-face dimerization of the anthracene units and radical reactions. Model anthracene photodimers are cleaved in solid films of PET by irradiation at 254 nm, but polymeric anthracene photodimerization reactions are irreversible under these conditions. The combination of irreversible anthracene photodimerization and irreversible radical reactions renders the cross-links permanent.

Introduction

Polyesters derived from aromatic acids and aliphatic diols such as poly(ethylene terephthalate) (PET) and poly(ethylene naphthalenedicarboxylate) (PEN) have desirable thermomechanical properties.[1] The enhanced properties of PEN over those of PET led us to investigate the effects of the larger arene units on the physical properties of copolyesters. We have previously reported on the physical and chemical properties of poly(ethylene terephthalate-*co*-2,6-anthracenedicarboxylate) whereby we used Diels−Alder chemistry to add suitable dienes across the 9- and 10-positions of the anthracene units. Use of bis(maleimide)s led to rapid, irreversible cross-linking.[2]

Reversible cross-links may be thermally or photochemically labile. Thermally reversible interchain interactions include ionic attraction,[3,4] microphase separation of hard and soft segments,[5] and hydrogen bonding.[6] Thermally reversible cross-links can also be made by formation of labile covalent bonds. For example, polymers bearing dienes and dienophiles undergo reversible cross-linking reactions,[7] and nitroso-substituted polymers undergo gelation upon formation of nitroso dimers.[8] Other reactions that have been used as mechanisms for cross-linking include anhydride exchange,[9,10] complex formation,[11] and disulfide formation.[12]

Photochemically labile interactions are also used to reversibly cross-link polymers. Polyoxazolines with pendant coumarin groups are cross-linked through [2 + 2] cycloaddition reactions upon irradiation at wavelengths greater than 300 nm.[13] The cross-links are cleaved by irradiation at 253 nm. In another study, cross-linked polymer gels were prepared by polymerizing a mixture of butyl methacrylate with photoreactive acyloxime-containing bis(methacrylate)s.[14] The acyloxime cross-links are cleaved upon exposure to UV radiation.

In an attempt to provide processable polyesters with enhanced properties for use as synthetic fibers, packaging film, and tire cord, we sought to incorporate a reversible cross-linking mechanism into poly(ethylene terephthalate), PET. Functional comonomers for use in PET must be able to withstand the high temperatures required for the thermal transesterification polymerization of dimethyl terephthalate (or terephthalic acid) and ethylene glycol. In particular, cross-linking units should not undergo irreversible thermally promoted radical reactions. We chose to investigate dimethyl 2,6-anthracenedicarboxylate as a new comonomer for PET to study reversible photochemical cross-linking. The anthracene unit is aromatic and thermally stable. Anthracene photodimerizes through the 9- and 10-positions upon irradiation with light at wavelengths greater than 300 nm.[15] The photodimer cleaves upon exposure to wavelengths less than 300 nm or upon heating. The photodimerization of a number of substituted anthracenes with both electron-withdrawing and -donating groups has been investigated.[16]

Anthracene photodimerization has been used to chain extend and cross-link polymers. (9-Anthryl)methyl ether groups attached to one end of polystyrene chains undergo dimerization upon irradiation in solution at 366 nm to double the molecular weight.[17] When irradiated at 280 nm in solution, the original anthracene-terminated polystyrene is regenerated. Other studies of the cross-linking of anthracene-containing polymers do not attribute the cross-linking solely to face-to-face dimerization of the anthracene units. Thin films of copolymers derived from (anthracenyl)methyl methacrylate derivatives are irradiated to give cross-linked materials of interest as photoresists.[18] Cross-linking is attributed to radical processes arising from photolysis of the endoperoxide of the anthracene formed by reaction of the anthracene and oxygen as well as to photodimerization. In our work, we attempted to extend this photochemical cross-linking to condensation polymers (e.g., PET) through the synthesis and copolymerization of 2,6-anthracenedicarboxylic acid.

Experimental Section

Materials. All starting materials and solvents were purchased from the Aldrich Chemical Co. with the following exceptions: ethylene glycol, dimethyl terephthalate, $Mn(CH_3CO_2)O_2{\cdot}4H_2O$, and Sb_2O_3 were obtained from Hoechst Celanese/

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Table 1. Composition and Characterization of Copolymers

	monomer feed				polymer characterization				
copolymer	DMT, g (mol)	**8**, g (mmol)	mol % **8**	mol % anthracene-dicarboxylate	T_g/°C	ΔC_p/J/g°C	T_m/°C	ΔH_m/J/g	% crystallinity
PET[c]	777 (4.00)	0	0	0	80	0.25	266	25.9	20.6
PET-2A[c]	777 (4.00)	12 (41)	1	1.6	86	0.11	252	29.3	23.4
PET-4A[d]	9.7 (0.05)	0.74 (2.5)	5	4.2	85	0.28	236	30.7	24.5
PET-18A[d]	9.7 (0.05)	2.9 (10)	20	18	95	0.23			

[a] Determined by ^{1}H NMR integration; see Discussion section. [b] Determined from measurement of ΔH_m (Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973). [c] Prepared by large-scale ester interchange; see Experimental Section. [d] Prepared by small-scale ester interchange; see Experimental Section.

Trevira Corp. Polymer thin films were spin-coated on glass slides from 10% polymer solutions in trifluoroacetic acid, unless otherwise noted. Samples were irradiated as thin films or in solution in a Rayonet chamber reactor (RPR-200) with 16 RPR-2537 Å or RPR-3500 Å bulbs. Solutions were irradiated in the absence of oxygen after three freeze/thaw cycles. Thin films were irradiated in air or under a flow of nitrogen in a quartz tube.

Characterization. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on 300 MHz Varian Gemini 2000 and 500 MHz Bruker DMX instruments. Polymer samples were dissolved in 3:1 (v/v) mixture of trifluoroacetic acid (TFA) and $CDCl_3$. ^{13}C NMR spectra were recorded on a Varian Gemini instrument at 75 MHz. UV−vis spectroscopy was performed using a Perkin-Elmer Lambda 19 spectrometer. Infrared spectroscopy was performed using a Nicolet 520 FTIR. Melting points were determined using a Thomas-Hoover melting point apparatus. Differential scanning calorimetry (DSC) was performed under nitrogen using a Perkin-Elmer series 7 differential scanning calorimeter. The temperature program provided heating and cooling cycles between 50 and 300 °C at 10 °C/min. Samples were analyzed for glass transition temperature, T_g, and melting point, T_m. Dilute solution viscometry was performed at 25 °C using ~1.5 wt % polymer solutions in 2-chlorophenol. Flow times were measured for five trials and averaged. Single point intrinsic viscosities were calculated on the basis of the method of Solomon and Cuita.[19] Molecular weights were estimated using K (6.56×10^{-4} dL/g) and a (0.73) values for PET.[20]

Dimethyl 2,6-Anthracenedicarboxylate, 1. Dimethyl 2,6-anthracenedicarboxylate, **1**, was synthesized in six steps[2] and isolated as a bright yellow solid; mp 274−276 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 2H, Ar−$H_{9,10}$); 8.57 (s, 2H, Ar−$H_{1,5}$); 8.03 (m, 4H, Ar−$H_{3,4,7,8}$); 4.00 (s, 6H, CH_3). IR (KBr): 3026 (Ar C−H stretch), 2967 (C−H stretch), 1716 (C═O stretch), 1440, 1328, 1249 (C−O stretch), 1091, 762 cm^{-1}. Elemental Analysis Calcd for $C_{18}H_{14}O_4$: C, 73.45%; H, 4.80%. Found: C, 72.90%; H, 4.98%.

Dioctyl 2,6-Anthracenedicarboxylate, 2. Reaction of **1** (5.0 g, 17 mmol) and lithium octyloxide (6.8 g, 50 mmol) gave **2** as a bright yellow solid;[2] mp 112−116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 2 H, Ar−$H_{9,10}$); 8.59 (s, 2H, Ar−$H_{1,5}$); 8.06 (m, 4 H, Ar−$H_{3,4,7,8}$); 4.41 (t, 4 H, J = 6.6 Hz, C1 CH_2); 1.84 (m, 4 H, C2 CH_2); 1.4 (m, 20 H); 0.89 (t, 6 H, J = 6.6 Hz, CH_3). IR (KBr): 2921 (Ar C−H stretch), 2855 (C−H stretch), 1723 (C═O stretch), 1249 (C−O stretch), 762 cm^{-1}. Elemental Analysis Calcd for $C_{32}H_{42}O_4$: C, 78.31%; H, 8.64%. Found: C, 78.17%; H, 8.69%.

Dioctyl 2,6-Anthracenedicarboxylate Dimer, 3. A solution of dioctyl 2,6-anthracenedicarboxylate, **2** (0.30 g, 0.61 mmol), in chloroform (30 mL) in a 50 mL Pyrex round-bottom flask was irradiated at 350 nm for 24 h. The contents were concentrated under reduced pressure. Column chromatography (silica gel, CH_2Cl_2) and recrystallization from hexanes gave the dimer of dioctyl 2,6-anthracenedicarboxylate, **3**, as a white solid (98 mg, 33% yield); mp 142−144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (s, 4 H, Ar−$H_{1,1',5,5'}$); 7.54 (d, 4 H, J = 7.7 Hz, Ar−$H_{3,3',7,7'}$); 7.02 (d, 4 H, J = 7.7 Hz, Ar−$H_{4,4',8,8'}$); 4.72 (s, 4H, C 9,9′,10,10′); 4.18 (t, 8H, J = 6.6 Hz, C1 CH_2); 1.68 (m, 8 H, C2 CH_2); 1.27 (m, 40 H); 0.86 (t, 12 H, J = 6.6 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (C═O), 147.8, 124.5, 128.4, 128.1, 128.0, 121.1, 64.9 (O−CH_2), 53.0 (C 9,9′,10,10′), 31.6, 29.1, 29.0, 28.4, 25.8, 22.5, 13.9. IR (KBr): 2960 (Ar C−H stretch), 2934 (C−H stretch), 2848 (C−H stretch), 1723 (C═O stretch), 1611, 1275, 1111, 782, 610 cm^{-1}. MS (EI): 981 (M$^+$), 925, 852, 490, 361. Elemental Analysis Calcd for $C_{64}H_{84}O_8$: C, 78.31%; H, 8.64%. Found: C, 78.09%; H, 8.68%. UV−vis (hexanes): λ_{max} 237 nm, log ϵ = 4.98.

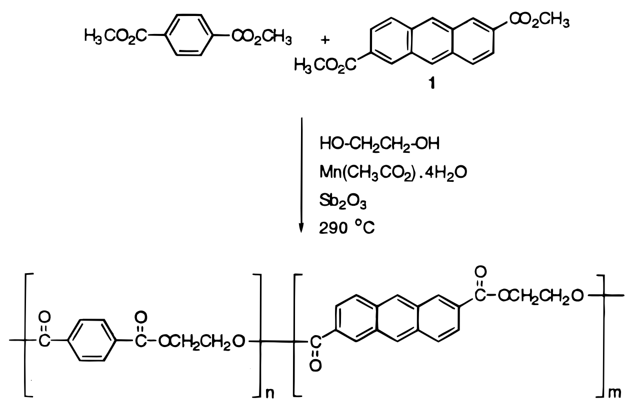


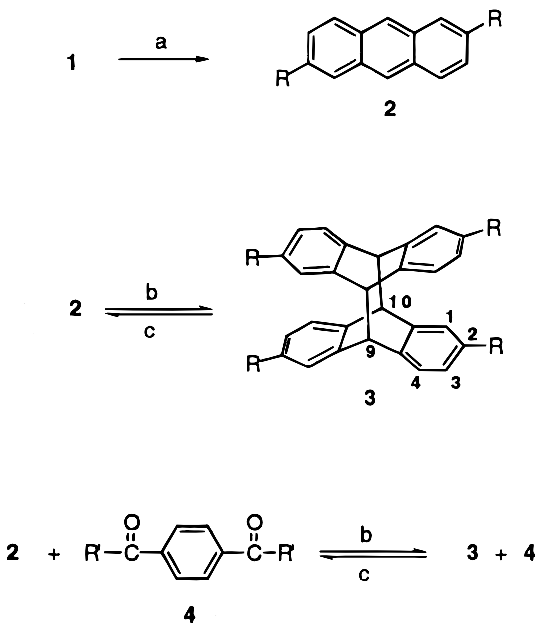
Figure 1. Synthesis of poly(ethylene terephthalate-*co*-2,6-anthracenedicarboxylate), PET-A.

PET−Anthracene Copolymers. PET containing 4 and 18 mol % of the 2,6-anthracenedicarboxylate structural unit (PET-4A and PET-18A, respectively) were prepared by small-scale thermal ester interchange in a round-bottom flask.[2] The PET and the copolymer containing 2 mol % of the 2,6-anthracenedicarboxylate structural unit (PET-2A) were prepared by large-scale ester interchange in a stirred stainless steel reaction vessel[2] (Table 1).

Results and Discussion

Monomer Synthesis. Dimethyl 2,6-anthracenedicarboxylate, **1**, was synthesized by a previously published route.[2] Briefly, Friedel−Crafts acylation of *p*-xylene with *p* -toluoyl chloride followed by a thermally promoted Elbs reaction gave a mixture of 2,6-dimethylanthracene and 2,6-dimethyl-9(10*H*)-anthracenone. The mixture was oxidized with an excess of chromium trioxide to give 2,6-anthraquinonedicarboxylic acid, which was reduced with zinc in aqueous ammonium hydroxide at reflux to provide 2,6-anthracenedicarboxylic acid. Treatment with iodomethane and lithium carbonate in DMF gave the corresponding dimethyl ester **1**. The dioctyl ester was prepared by treatment of **1** with lithium octyloxide.

Polymer Synthesis. Melt polymerization of dimethyl terephthalate, dimethyl 2,6-anthracenedicarboxylate, **1**, and ethylene glycol gave copolymers of PET containing the 2,6-anthracenedicarboxylate structural unit (Figure 1). Manganese acetate catalyzes the initial ester interchange in which methanol (from dimethyl terephthalate) is displaced by ethylene glycol. In the second stage



R = $CO_2(CH_2)_7CH_3$, R' = $OCH_2CH_2OCH_3$ (a) 1-BuLi, 1-octanol, THF, rt, 24 h; (b) HFIP, 350 nm, 3 h; (c) HFIP, 254 nm, 3 h.

Figure 2. Model compound photochemistry: synthesis of model compounds **2** and **3**.

of polymerization, the elimination of ethylene glycol is catalyzed by antimony trioxide. Three different copolymer compositions were synthesized. The compositions of the polymers were determined by comparison of the integrals of the ^{1}H NMR spectrum for the singlets at 8.97 and 8.71 ppm (corresponding to two protons each; C-9,10 and C-1,5 of the anthracene unit, respectively) to the singlet at 8.23 ppm (corresponding to the four equivalent protons of the terephthalate structural unit). The copolymer compositions were in accord with the monomer feed ratio (Table 1).

The polymers were analyzed by DSC to determine the glass transition temperature, T_g, and the melting temperature, T_m. DSC thermograms of the copolymers demonstrate that they are thermally stable to cycling from 50 to 300 °C. As shown in Table 1, the percentage of 2,6-anthracenedicarboxylate units has an effect on the thermal properties of the copolymers. As the amount of incorporated anthracene increases, the T_g increases and the T_m decreases. The increase in T_g is attributed to the rigid anthracene units that enhance chain stiffness and thus increase the temperature needed for the onset of segmental motion. The decrease in melting temperature is due to a disruption of crystallinity by the anthracene units. The copolymer containing 18% of the anthracene structural unit, i.e. PET-18A, does not display a melting endotherm. The high concentration of anthracenedicarboxylate units prevents crystallization.

Model Reactions. To conduct model studies on the photochemical dimerization of the anthracenedicarboxylate unit of the copolymers, we prepared the dioctyl ester **2** (Figure 2). The dioctyl ester is soluble in a wide variety of organic solvents whereas the dimethyl ester is only sparingly soluble. Irradiation of a solution of **2** in $CHCl_3$ (0.02 M) at 350 nm provided the anthracene photodimer, **3**. The ^{1}H NMR of **2** consists of two singlets at 8.81 and 8.59 ppm corresponding to the protons on C-9,10 and C-1,5 of the anthracene ring, respectively. The remaining aromatic protons on C-3,4,7,8 give a multiplet at 8.06 ppm. The ^{1}H NMR of the photodimer, **3**, in contrast, has a singlet at 7.59 ppm representing the aromatic protons on C-1,1′,5,5′ (for clarity, the carbons on the dimer are numbered according to the assignment of positions of the monomeric anthracene; see Figure 2) and two doublets at 7.54 and 7.02 ppm corresponding to the protons on C-3,3′,7,7′ and C-4,4′,8,8′. A singlet at 4.72 ppm is attributed to the four bridgehead protons (C-9,9′,10,10′).

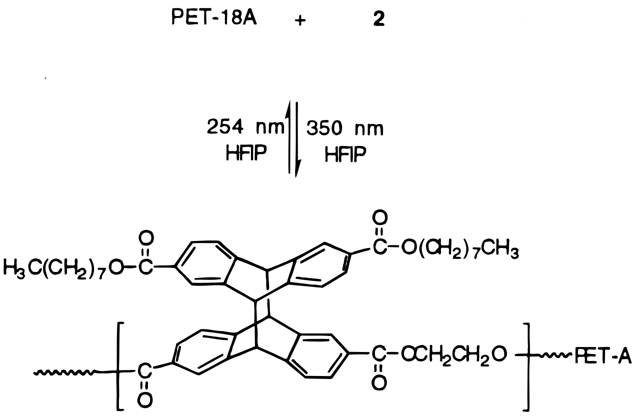


Figure 3. Face-to-face photodimerization of model compound **2** with the anthracene units in PET-18A.

Photodimers of anthracene are cleaved photochemically by irradiation at wavelengths below 300 nm and thermally. Irradiation of a solution of **3** in $CHCl_3$ (0.02 M) for 1.5 h at 254 nm regenerated **2** (50% conversion, determined by ^{1}H NMR spectroscopy). Similarly, heating **3** neat at 145 °C for 12 h gave **2** (95% conversion).

To demonstrate that the anthracene units of the polymer undergo face-to-face reaction, a solution of PET-18A (0.1 g) and **2** (0.036 g) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (7 mL) was irradiated at 350 nm for 4 h (total anthracene concentration ~0.02 M) (Figure 3). The solvent was removed, and the solids were extracted with THF in a Soxhlet extractor to remove unreacted dioctyl anthracene, **2**, and its photodimer, **3**. The ^{1}H NMR spectrum of the remaining polymer ($CDCl_3$/TFA) showed a multiplet at 7.65 ppm and a doublet at 7.15 ppm that were assigned to the protons of the polymeric photodimer. Integration of the peaks in the ^{1}H NMR spectrum indicates that 27% of the polymer anthracene units had reacted with **2**. The lack of precipitation during this irradiation and the solubility of the product indicate that the product is not heavily cross-linked. This suggests that the polymeric photodimer is formed primarily by reaction of the dioctyl ester, **2**, with 2,6-anthracenedicarboxylate structural units in PET-A, rather than by cross-linking of two polymer structural units. This photodimerization is reversible: irradiation of the polymer in HFIP solution at 254 nm for 7 h led to a 90% decrease in the signals of the photodimer, and the original singlets for the anthracene units at 9.0 and 8.7 ppm increased in intensity. This shows that the anthracenedicarboxylate units in PET-A undergo reversible photocycloaddition reactions in solution.

Cross-Linking of PET-A. Irradiation of spin-coated films of PET-4A and PET-18A at 350 nm in air for 1 h affords a polymer that gels in trifluoroacetic acid, but does not dissolve, suggesting the formation of a cross-linked material. UV−vis spectroscopy of the irradiated films shows a decrease in the absorbance of anthracene.

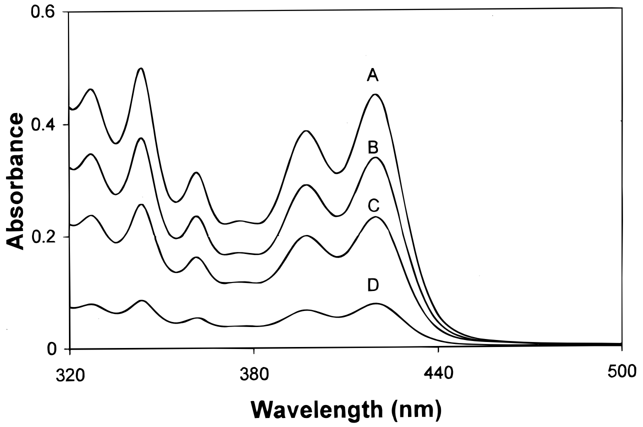


Figure 4. UV–vis spectra of PET-4A spin-coated films: (A) original film; (B) film irradiated for 5 min at 350 nm under air (25% loss); (C) film irradiated for 10 min at 350 nm under air 49% loss; (D) film irradiated for 1 h at 350 nm (90% loss).

Table 2. Cross-Linking of PET-A Films by Irradiation at 350 nm

	irradiation time[a] (min)	UV–vis[b] % anthracene loss	$[\eta]$ (dL/g)	M_v[c] (10^3 g/mol)
PET	0	0	0.58 ± 0.01	11
PET	10	0	0.58 ± 0.01	11
PET-4A	0	0	0.64 ± 0.01	12
PET-4A	5	25	1.07 ± 0.01	25
PET-4A	10	49	1.21 ± 0.01	30

[a] Determined by ^{1}H NMR integration; see Discussion section. [b] Determined from measurement of ΔH_m (Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973). [c] Prepared by large-scale ester interchange; see Experimental Section. [d] Prepared by small-scale ester interchange; see Experimental Section.

When PET-4A is irradiated for at 350 nm for 5 min in air, a 25% decrease in the anthracene absorbance at 420 nm is observed, while irradiation for 10 min causes a 49% decrease, and a 90% decrease is observed after 1 h (Figure 4).

Dilute solution viscometry was used to investigate the effect of irradiation on the molecular weight of PET-A prior to gelation. PET-4A films were irradiated at 350 nm in air for various times (0, 5, and 10 min). Viscosity measurements were conducted on ~1.5 wt % solutions in 2-chlorophenol at 25 °C using an Ubbelohde viscometer. The single point intrinsic viscosity of each sample was determined using the method of Solomon and Cuita.[18] The single point viscometry of PET-4A of 0.64 dL/g corresponds to a molecular weight of 12×10^3 g/mol (using PET constants $K = 6.56 \times 10^{-4}$ dL/g, $a = 0.73$).[19] As shown in Table 2, the viscosity increases to 1.07 dL/g (25×10^3 g/mol) upon irradiation for 5 min and to 1.21 dL/g (30×10^3 g/mol) after irradiation for 10 min. The material gels in 2-chlorophenol when the copolymer films are irradiated for 15 min.

Thermal Analysis of Irradiated PET-A. PET-4A ($T_m = 236$ °C), irradiated at 350 nm in air for 1 h, gives a melting point of 219 °C, indicating that formation of cross-links disrupts crystallinity (Figure 5). However, no crystallization exotherm appears upon cooling from the melt. The melting transition does not appear in the second heating cycle. This can be attributed to the cross-links impeding crystallization and is consistent with cross-linking in the amorphous regions of the polymer. As shown in Figure 6, irradiation of PET-2A at 350 nm in air for 1 h shows that polymers with a lower concentration of anthracene units undergo cross-linking to afford materials in which crystallization is impeded to a smaller extent. The melting transition is present during the first heating curve and decreases in the second and third heating curves.

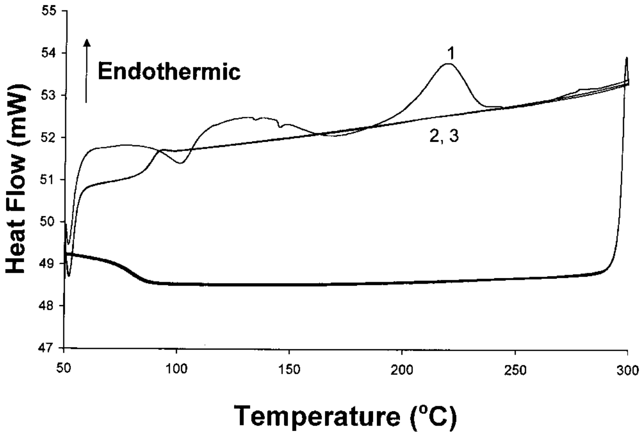


Figure 5. DSC thermogram of PET-4A cross-linked by irradiation at 350 nm for 1 h. See Experimental Section. Heating rate = 10 °C/min. Three heating–cooling cycles are shown.

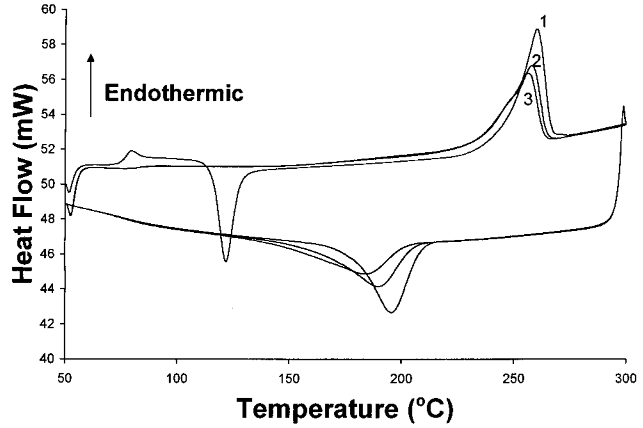


Figure 6. DSC thermogram of PET-2A cross-linked by irradiation at 350 nm for 1 h. See Experimental Section. Heating rate = 10 °C/min. Three heating–cooling cycles are shown.

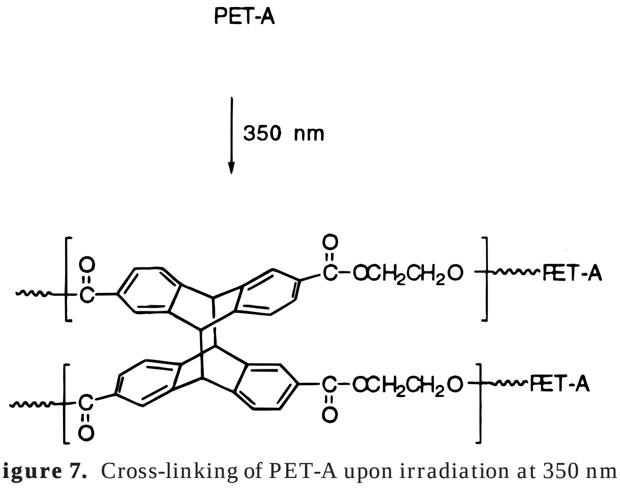


Figure 7. Cross-linking of PET-A upon irradiation at 350 nm.

Reversibility. Although we set out to demonstrate that cross-linking of PET-A could be attributed to anthracene photodimerization (Figure 7), we have been unable to confirm the structure of the cross-link. Cleavage of the cross-links by irradiation at 254 nm, or heating at 145 °C (see Model Compounds section), would provide strong evidence for the anthracene photodimer cross-link. However, cross-linked films exposed to these conditions did not return the polymers to their original form. Reversible cross-linking experiments were also attempted in solution. When solutions of PET-4A and PET-18A in HFIP (10% w/v) were irradiated at 350 nm (in the absence of air), insoluble films formed on the cuvette walls. However, subsequent irradiation of the sample at 254 nm failed to render the material soluble. The lack of reversibility of the cross-linking observed upon the irradiation of both solutions and thin films could possibly be due to the absorbance of the terephthalate chromophore at 254 nm that prevents that light from reaching the photodimer, quenching of the excited-state anthracene photodimer by the terephthalate units, a cage effect that locks in the structure of the photodimer, or radical processes other than photodimerization that lead to cross-linking. The following experiments were designed to address these issues.

If anthracene dimerization is the cross-linking mechanism, then the inability to cleave the photodimer cross-links could be attributed to the strong absorbance of terephthalate groups of PET in the 254 nm region or quenching of the excited-state photodimer by the terephthalate groups. To examine the photodimerization in the presence of an excess of terephthalate chromophores, a solution of **2** (0.018 M) and a 5-fold excess of bis(2-methoxyethyl) terephthalate (**4**) (0.09 M) in HFIP was irradiated at 350 nm for 3 h (Figure 2). ^{1}H NMR spectroscopy showed the formation of a mixture of the dimer **3** (50% conversion) and unreacted **2**. Subsequent irradiation of this solution at 254 nm for 4.5 h cleaved the photodimer to give a mixture of 13% **3** and 87% **2**. Both the forward and reverse reactions occur without the formation of side products. Thus, although the terephthalate units absorb light at 254 nm, there is sufficient light of this wavelength to cleave the photodimer in solution, and the terephthalate units do not quench the excited-state photodimer. Films were render insoluble and unswellable after very short reaction times (minutes), making it difficult to determine of the extent of cross-linking and to correlate this with the consumption of anthracene units. However, given the continued decrease in absorbance of the polymers at long reaction times (after the material is rendered rigid), it is clear that processes other than dimerization are responsible for the consumption of the anthracene units.

To examine cleavage of the photodimer in the presence of PET in the solid state, spin-coated films of solutions of PET (0.2 g) and the model photodimer, **3** (0.1 g), in HFIP (3 mL) were irradiated at 254 nm. UV−vis spectra of films irradiated in both air and nitrogen showed the appearance of the anthracene absorption ($A = 0.220$ at 420 nm). Therefore, cleavage of the model anthracene photodimer does occur in solid PET, and the excited-state photodimer is not quenched by the terephthalate groups. Thus, the reverse photochemical reaction occurs on model compounds in solution and in the solid state.

The inability to un-cross-link irradiated films of PET-A might be attributed to a cage effect that locks in the structure of the photodimer. To examine photodimer cleavage in the solid state, PET-18A with 27% of the anthracene units photodimerized with **2** (see Model Compounds section) was spin-coated on glass slides and irradiated at 254 nm for 30 min both in air and under nitrogen. UV−vis spectroscopy showed a further 45% *decrease* in anthracene absorbance at 420 nm after irradiation in air and a 2% loss for the film under nitrogen. No dioctyl ester, **2**, was extracted with THF in a Soxhlet extractor. This suggests that photocleavage of the polymeric photodimer *does not occur in the solid state* or that there is a rapid consumption of liberated anthracene by another process. Lack of photocleavage may be due to a cage effect, whereby the structure of the photodimer is locked in by the polymer chains.

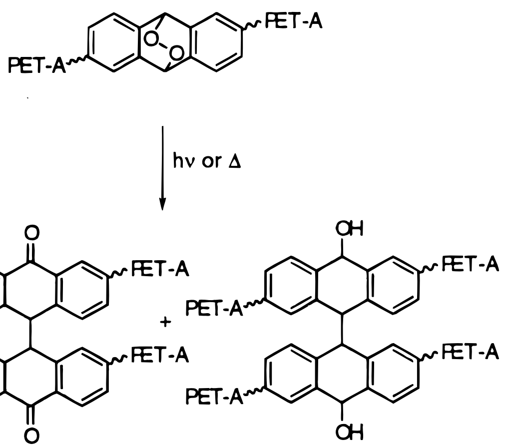


Figure 8. Decomposition of anthracene-9,10-endoperoxide to give dimerized products other than the face-to-face anthracene dimer.

Model compounds irradiated in HFIP were studied in order to determine whether any products other than the photodimer are formed in solution. ^{1}H NMR spectroscopy of a solution of **2** in HFIP (0.02 M) irradiated at 350 nm for 3 h in the absence of air showed that the photodimer, **3**, is the only product formed (Figure 2). This solution of **2** and **3** was then irradiated at 254 nm for 3 h. ^{1}H NMR of the resulting mixture showed that the photodimerization is reversible in solution, and no side products were identified in either reaction.

PET-A films were irradiated to study photochemistry in the solid state. PET-18A films irradiated at 350 nm in air for 30 min show a 75% anthracene loss (by UV−vis absorption), while under nitrogen only a 27% loss is observed. Further irradiation of the same films for an additional 30 min gives an 87% loss (total) of anthracene in air and a 44% loss under nitrogen. Irradiation of these same films at 254 nm for 1 h in air shows an additional 6% *loss* of anthracene and a 4% *loss* is observed under nitrogen. Thus, there is a faster consumption of the anthracene in air than under nitrogen, and the cross-linking reaction is not reversible upon irradiation at 254 nm. The greater loss of anthracene in air could be due to the formation of the anthracene-9,10-endoperoxide. This endoperoxide can undergo irreversible thermal or photochemical decomposition, which leads to cross-linked polymer chains and a number of oxidized products (Figure 8).[22] Thus, the cross-linking of PET-A could be a result of the irreversible radical reactions other than photodimerization. Some evidence for formation of species other than the photodimer was obtained upon irradiation of PET-2A films in air for 1 h at 350 nm. These films remained soluble, and the ^{1}H NMR recorded in TFA/CDCl$_3$ showed a loss of anthracene (8.97 and 8.71 ppm) and the appearance of a new signal at 7.8 ppm. This signal is not due to the anthracene photodimer and remains unassigned.

Conclusion

We have demonstrated an irreversible photo-cross-linking of PET copolymers containing the 2,6-anthracenedicarboxylate structural unit. The cross-linking is attributed to a combination of face-to-face dimerization of anthracene and radical reactions. We have demonstrated that a model anthracene photodimer can be cleaved in solid films of PET by irradiation at 254 nm, but polymeric photodimers cannot be cleaved under these conditions. The combination of irreversible anthracene photodimerization and irreversible radical reactions renders the cross-links permanent. However, this process provides a useful treatment for cross-linking prefabricated films or fibers.

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