Cross-Linking and Modification of Poly(ethylene terephthalate-*co*-2,6-anthracenedicarboxylate) by Diels−Alder Reactions with Maleimides

Jeffrey R. Jones,[†] **Charles L. Liotta,**[†] **David M. Collard,***[,†] **and David A. Schiraldi**[‡]

School of Chemistry and Biochemistry and the Polymer Education and Research Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, and KoSa, P.O. Box 5750, Spartanburg, South Carolina 29304-5750

Received April 26, 1999; Revised Manuscript Received June 28, 1999

ABSTRACT: Poly(ethylene terephthalate) (PET) copolymers containing 2,6-anthracenedicarboxylate structural units are modified by Diels−Alder reactions with maleimides. Low molecular weight bis(maleimide)s are used to chain extend and cross-link the polymers. The resulting materials were characterized by ^{1}H NMR, UV−vis, DSC, and dilute solution viscometry. The Diels−Alder reaction of low molecular weight anthracenes and maleimides is thermally reversible at 250 °C. However, the reverse reaction is slow, and the PET−anthracene copolymers are prone to thermal decomposition at these higher temperatures.

Introduction

The modification of macromolecules by grafting reactions provides an opportunity to change physical and chemical properties of polymers.[1] Modification of poly(ethylene terephthalate), PET, is desirable in order to enhance properties such as hydrophilicity, soil resistance, and dyeability.[2] However, attempts to prepare functional PET copolymers onto which groups can be grafted is severely limited by the conditions for the polymerization. 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, the functional units should not undergo irreversible thermally promoted radical reactions.

Chain extension and cross-linking of PET can be achieved by reaction of functional end groups with difunctional compounds. Examples of chain extenders that undergo addition reactions with end groups without the formation of byproducts include diepoxides,[3] diisocyanates,[4] bis(oxazoline)s,[5] bis(benzoxazinone)s,[6] and bis(*N*-acyllactam)s.[7] PET has also been cross-linked by photochemical methods using cross-linking agents incorporated into the polymer backbone such as phenylene bis(acrylate)s[8] and cross-linking agents that are blended after polymerization such as *N*-allylphthalimide.[9] Other approaches to provide thermoset PET include transesterification of pendant hydroxyl groups.[10]

The mechanical properties and processing behavior of thermoplastics depend critically on the average size and distribution of sizes of macromolecules. Although high molecular weight polymers have desirable mechanical properties, this is often achieved at the expense of the ease of processing (i.e., high melt and solution viscosities). A number of approaches have been developed to incorporate thermally or photochemically reversible cross-links to provide cross-linked materials that are thermally processable. These methods offer the possibility of enhancing mechanical properties after fabrication of fibers, films, and coatings, while retaining the possibility of refabrication and recycling. Thermally reversible interactions used to increase interchain interactions include hydrogen bonding[11] and ionic attraction.[12] Methods of cross-linking by making covalent bonds include formation of anhydrides[13] and dimerization of nitroso groups.[14] In an attempt to provide processable polyesters with enhanced properties for use as synthetic fibers and packaging film, we sought to incorporate a reversible cross-linking mechanism into PET.

Thermally reversible Diels−Alder [4 + 2] cycloadditions of a diene and dienophile[15] have been used to prepare and modify polymers. In pioneering work, Stille polymerized bis(maleimide)s and bis(cyclopentadiene)s by cycloaddition.[16] Reversible Diels−Alder polymerizations using monomers such as difurufuryl adipate and bis(maleimido)diphenylmethane[17] have since been demonstrated. Dienes and dienophiles have also been attached as pendants or end groups on polymer backbones. For example, reversible cross-linking through a Diels−Alder reaction was demonstrated by blending furan-substituted and maleimide-substituted poly(*N*-acetylethylenimine)s.[18] In other studies, dienes have been incorporated as pendant groups, and the polymer has been cross-linked with low molecular weight bis(dienophile)s. Various bis(maleimide)s reversibly cross-link and chain extend polymers with pendant furan groups[19] and 1,3-diene units in the main chain.[20]

We chose to investigate dimethyl 2,6-anthracenedicarboxylate as a new comonomer for PET to allow us to study grafting and reversible cross-linking by the Diels−Alder reaction. The anthracene unit is aromatic and thermally stable. Anthracene acts as a diene in Diels−Alder reactions with a variety of dienophiles, and the retro-Diels−Alder reaction of these adducts has also been investigated.[21] Substitution of the anthracene with two carboxylate groups affords a monomer that is compatible with the preparation of PET.[22] In this paper, we report the preparation of poly(ethylene terephtha-

---

[†] Georgia Institute of Technology.

[‡] KoSa.

* Author for correspondence.

10.1021/ma990638z CCC: $18.00

late-*co*-2,6-anthracenedicarboxylate) and the Diels–Alder reactions with maleimides, which open new avenues for modification of commercially important polyesters. Reaction with a bis(maleimide) results in chain extension and cross-linking.

Experimental Section

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

Characterization. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on 300 MHz Varian Gemini 2000 and Bruker DMX 500 MHz 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 Lamda 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 T_g and 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.[23] Molecular weights were estimated using K and a values of 6.56×10^{-4} dL/g and 0.73, respectively.[24]

2,5,4′-Trimethylbenzophenone, 1.[25] The title compound was prepared by Friedel–Crafts acylation of *p*-xylene (69 g, 0.65 mol) with *p*-toluoyl chloride (100 g, 646 mmol) in CS_2 (150 mL) in the presence of $AlCl_3$ (100 g, 750 mmol). Workup and purification by distillation under vacuum (110–120 °C, 0.05 mmHg, lit. bp[25] 202 °C, 23 mmHg) gave 2,5,4′-trimethylbenzophenone, **1**, as a white solid (122.25 g, 84%); mp 50–53 °C (lit. mp[25] 54 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, 2H, J = 8.2 Hz, Ar–$H_{2',6'}$); 7.32 (d, 2H, J = 8.2 Hz, Ar–$H_{3',5'}$); 7.21 (m, 2H, Ar–$H_{3,4}$); 7.05 (s, 1 H, Ar–H_6); 2.36 (s, 3H, CH_3); 2.67 (s, 3H, CH_3); 2.12 (s, 3H, CH_3). IR (KBr): 3039, 2967, 2927, 2875, 1664, 1611, 1308, 1275, 834, 775 cm^{-1}.

2,6-Anthraquinonedicarboxylic Acid, 4. 2,5,4′-Trimethylbenzophenone, **1** (30 g, 0.13 mol), was heated at reflux (~360 °C) under air for 6 h and cooled.[25] The solid was triturated with ether (50 mL), and the insoluble portion was collected by vacuum filtration and washed with ether. The ether washings were added to the filtrate, and the ether was removed under reduced pressure to afford unreacted **1**. After repeating this process four times, 20 g of ether-insoluble material was collected. Recrystallization from carbon disulfide gave a 2:3 mixture of 2,6-dimethylanthracene, **2**, and 2,6-dimethyl-9(10*H*)-anthracenone, **3**, as a yellow solid (8.3 g). The crude mixture was used without further purification.

CrO_3 (59.4 g, 0.594 mol) was added to a well-stirred solution of sulfuric acid (2 mL), acetic anhydride (15 mL, 0.16 mol), and acetic acid (350 mL) cooled to 20 °C in a water–ice bath.[26] The mixture of 2,6-dimethylanthracene, **2**, and 2,6-dimethyl-9(10*H*)-anthracenone, **3** (11.6 g, ~54.0 mmol), was added in small portions, maintaining the reaction temperature below 35 °C in an ice–water bath. After the addition was complete, the mixture was stirred for 2 h while the temperature was kept below 35 °C and then heated to 120 °C for 3 h. The mixture was cooled to room temperature and poured into water (2 L), and the precipitate was removed by vacuum filtration. The yellow solid was washed with water and dried in a vacuum oven to afford 2,6-anthraquinonedicarboxylic acid, **4**, as a yellow solid (14.18 g, 89%); mp >300 °C (lit. mp[27] 360 °C). ^1H NMR (300 MHz, DMSO-d_6): δ 8.68 (s, 2H, Ar–$H_{1,5}$); 8.40 (d, 2H, J = 8.2 Hz, Ar–$H_{3,7}$); 8.32 (d, 2H, J = 8.2 Hz, Ar–$H_{4,8}$). IR (KBr): 3460, 3045, 1703, 1611, 1288, 722 cm^{-1}.

Dimethyl 2,6-Anthracenedicarboxylate, 8. A mixture of **4** (30.2 g, 0.102 mol), $CuSO_4$ (0.8 g, 5 mmol), Zn^0 (94.2 g, 1.44 mol), and concentrated NH_4OH (715 mL) was heated at reflux for 4 h.[28] Additional NH_4OH (715 mL) was added dropwise throughout this period. The mixture was cooled and vacuum filtered, and the filtrate was acidified with 12 M HCl to give a bright yellow precipitate. The precipitate was collected by vacuum filtration and dried in a vacuum oven to give a 1:2 mixture of 2,6-anthracenedicarboxylic acid, **5**, and 9,10-dihydro-2,6-anthracenedicarboxylic acid, **6**, as a bright yellow solid (26 g), which was used without further purification. 2,6-Anthracenedicarboxylic acid, **5**: ^1H NMR (300 MHz, DMSO-d_6) δ 8.88 (s, 2H, Ar–$H_{9,10}$); 8.82 (s, 2H, Ar–$H_{1,5}$); 8.20 (d, 2H, J = 8.8 Hz, Ar–$H_{3,7}$); 7.96 (d, 2H, J = 8.8 Hz, Ar–$H_{4,8}$). 9,10-Dihydro-2,6- anthracenedicarboxylic acid, **6**: ^1H NMR (300 MHz, DMSO-d_6) δ 7.91 (s, 2H, Ar–$H_{1,5}$); 7.78 (d, 2H, J = 8.0 Hz, Ar–$H_{3,7}$); 7.44 (d, 2H, J = 8.0 Hz, Ar–$H_{4,8}$); 4.05 (s, 4H, C–$H_{9,10}$).

A suspension of the mixture of **5** and **6** (27 g, ~0.10 mol), iodomethane (142 g, 1.00 mol), and lithium carbonate (74 g, 1.0 mol) in DMF (1300 mL) was stirred for 24 h.[29] The mixture was added to 1 M HCl (5 L), and the yellow precipitate was collected by vacuum filtration and dried in a vacuum oven to give a 2:1 mixture of 2,6-dimethyl 9,10-dihydroanthracenedicarboxylate, **7**, and dimethyl 2,6-anthracenedicarboxylate, **8** (24.5 g).

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (27 g, 0.12 mol) was added to the mixture of **7** and **8** in benzene (1 L), and the suspension was heated at reflux for 1 h. The mixture was cooled and vacuum filtered, and the solid was washed with methanol and dried in a vacuum oven to give dimethyl 2,6-anthracenedicarboxylate, **8**, as a bright yellow solid (22.3 g, 75% overall from **4**); mp 274–276 °C. ^1H 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). ^{13}C NMR (75 MHz, TFA-*d*): δ 173.2 (C=O), 135.4, 135.3, 134.0, 131.3, 131.0, 128.9, 125.8, 122.6, 118.9, 115.1, 111.3, 55.2 (O–CH_3). IR (KBr): 3026, 2967, 1716, 1440, 1328, 1249, 1091, 762 cm^{-1}. MS (EI): 294 (M^+), 263, 235. Elemental analysis calcd for $C_{18}H_{14}O_4$: C, 73.45%; H, 4.80%; Found: C, 72.90%; H, 4.98%. UV–vis ($CHCl_3$): λ_{max1} 413 nm, log ϵ = 3.70; λ_{max2} 390 nm, log ϵ = 3.67; λ_{max3} 359 nm, log ϵ = 3.76; λ_{max4} 341 nm, log ϵ = 3.91; λ_{max5} 325 nm, log ϵ = 3.73; λ_{max6} 277 nm, log ϵ = 5.31.

Dioctyl 2,6-Anthracenedicarboxylate, 9. 1-Butyllithium (20 mL of 2.5 M solution in hexanes, 50 mmol) was added dropwise to a solution of 1-octanol (6.6 g, 50 mmol) in THF (125 mL).[30] Dimethyl 2,6-anthracenedicarboxylate, **8** (5.0 g, 17 mmol), was added to the solution, and the mixture was stirred at room temperature under nitrogen for 24 h. The dark red solution was added to CH_2Cl_2 (200 mL) and washed with water (2 × 1 L). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was recrystallized from hexanes to afford dioctyl 2,6-anthracenedicarboxylate, **9**, as a yellow solid (5.35 g, 65% yield); mp 112–116 °C. ^1H 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, C-1-CH_2); 1.84 (m, 4 H, C-2-CH_2); 1.4 (m, 20 H, $(CH_2)_5$); 0.89 (t, 6 H, J = 6.6 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (C=O), 132.9, 131.9, 131.8, 128.7, 128.5, 128.3, 124.6, 65.4 (O–CH_2), 31.7, 29.2, 29.1, 28.6, 26.0, 22.5, 13.9. IR (KBr): 2921, 2855, 1723, 1249, 762 cm^{-1}. MS (EI): 490 (M^+), 361, 266. Elemental analysis calcd for $C_{32}H_{42}O_4$: C, 78.31%; H, 8.64%. Found: C, 78.17%; H, 8.69%. UV–vis ($CHCl_3$): λ_{max1} 413 nm, log ϵ = 3.90; λ_{max2} 390 nm, log ϵ = 3.83; λ_{max3} 360 nm, log ϵ = 3.82; λ_{max4} 342 nm, log ϵ = 3.96; λ_{max5} 326 nm, log ϵ = 3.79; λ_{max6} 277 nm, log ϵ = 5.40.

Diels–Alder Adduct of Dioctyl 2,6-Anthracenedicarboxylate and *N*-Phenylmaleimide, 11. A mixture of dioctyl 2,6-anthracenedicarboxylate, **9** (0.25 g, 0.51 mmol), and *N*-phenylmaleimide, **10** (0.09 g, 0.51 mmol), was heated at 125 °C under nitrogen for 12 h. Column chromatography (silica gel, CH_2Cl_2) gave the Diels–Alder adduct **11** as a white solid (0.21 g, 62%); mp 117–120 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H, Ar–H_5); 8.04 (s, 1H, Ar–H_1); 7.97 (m, 2H, N–Ph); 7.52 (d, 1H, J = 7.7 Hz, Ar–H_7); 7.46 (d, 1H, J = 7.7 Hz, Ar–

Table 1. Composition and Charactization of Copolymers

	monomer feed			composition[a]					
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,[b] %
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	17.6	95	0.23			

[a] Determined by ^{1}H NMR integration; see Discussion section. [b] Determined from measurement of ΔH_m (ref 23). [c] Prepared by large-scale ester interchange; see Experimental Section. [d] Prepared by small-scale ester interchange; see Experimental Section.

H_8); 7.28 (m, 3H, N−Ph); 6.54 (m, 2H, Ar−$H_{3,4}$); 5.04 (s, 2H, bridgehead H); 4.33 (m, 4H, C-1-CH_2); 3.41 (m, 2H, $H_{9,10}$); 1.78 (m, 4H, C-2-CH_2); 1.31 (m, 20 H, $(CH_2)_5$); 0.89 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3 (C=O), 166.2 (C=O), 166.1 (C=O), 145.9, 143.4, 140.8, 138.3, 131.2, 129.8, 129.6, 129.2, 128.9, 126.2, 125.5, 125.4, 124.5, 65.3 (O−CH_2), 46.4, 46.2, 45.7, 31.6, 29.1, 29.0, 28.6, 28.5, 25.9, 25.8, 22.5, 13.9. IR (KBr): 2953, 2934, 2855, 1716, 1387, 1262, 1170, 1098, 742 cm^{-1}. MS (CI): 664 (M$^+$), 535, 490, 434. Elemental analysis calcd for $C_{42}H_{49}O_2N$: C, 75.98%; H, 7.45%; N, 2.11%. Found: C, 75.92%; H, 7.40%; N, 2.18%. UV−vis (hexanes): λ_{max} 231 nm, log ϵ = 4.72.

1,1′-(1,6-Hexanediyl)bis(1*H*-pyrrole-2,5-dione), 12. Reaction of maleic anhydride (18 g, 0.18 mol) and hexamethylenediamine (10 g, 86 mmol) according to the procedure of Searle[31] gave **12** as a light brown solid; mp 140−141 °C (lit. mp[31] 140−141 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (s, 4H, vinyl H); 3.52 (t, 4H, N−CH_2); 1.59 (m, 2H, CH_2); 1.31 (m, 4H, CH_2). IR (KBr) 3112, 2947, 2861, 1697, 1426, 1131, 847, 702 cm^{-1}.

Diels−Alder Adduct of Dioctyl 2,6-Anthracenedicarboxylate and 1,1′-(1,6-Hexanediyl)bis(1*H*-pyrrole-2,5-dione), 13. A mixture of dioctyl 2,6-anthracenedicarboxylate, **9** (0.20 g, 0.41 mmol), and 1,1′-(1,6-hexanediyl)bis(1*H*-pyrrole-2,5-dione), **12** (50 mg, 0.20 mmol), was heated at 125 °C under nitrogen for 15 h. Column chromatography (silica gel, CH_2Cl_2) and recrystallization from THF/MeOH gave the Diels−Alder adduct **13** as a white solid (50 mg, 20%); mp 192−198 °C. ^{1}H NMR (500 MHz, TFA/$CDCl_3$): δ 8.18 (s, 2H, Ar−H); 8.07 (s, 2H, Ar−H); 8.02 (m, 4H, Ar−H); 7.63 (d, 2H, J = 7.8 Hz, Ar−H); 7.54 (m, 2H, Ar−H); 5.09 (s, 4H, $H_{9,10}$); 4.46 (m, 8H, C-1-CH_2); 3.58 (s, 4H, N−CH_2); 3.19 (s, 4H, bridgehead H); 1.88 (m, 8H, C-2-CH_2); 1.37 (m, 40 H, $(CH_2)_5$); 0.94 (m, 12H, CH_3); 0.85 (s, 6H, $(CH_2)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2 (C=O), 166.3 (C=O), 166.1 (C=O), 146.2, 143.5, 141.1, 138.3, 129.6, 129.5, 129.0, 126.1, 125.3, 124.4, 65.3 (O−CH_2), 46.1, 45.5, 38.2, 31.7, 29.1, 28.6, 26.5, 25.9, 25.4, 22.5, 13.9. IR (KBr): 2927, 2861, 1703, 1249, 1170, 1097, 781 cm^{-1}. MS (FB): 1257 (M + H)$^+$, 1202, 1128, 1016. Elemental analysis calcd for $C_{78}H_{100}O_{12}N_2$: C, 74.48%; H, 8.03%; N, 2.23%. Found: C, 73.93%; H, 7.87%; N, 2.48%.

PET−Anthracene Copolymers.[32] The PET homopolymer and the copolymer containing 2 mol % of the 2,6-anthracenedicarboxylate structural unit (PET-2A) were prepared by the following method. Dimethyl terephthalate, dimethyl 2,6-anthracenedicarboxylate, **8**, ethylene glycol (521 g, 8.40 mol), Mn(CH_3CO_2)$_2$·4H_2O (0.277 g, 1.29 mmol), and Sb_2O_3 (0.358 g, 1.23 mmol) (Table 1) were added to a 1 L stainless steel reaction vessel equipped with a mechanical stirrer, distillation head, and condenser. The mixture was heated for 2 h at 180−210 °C, during which methanol was removed by distillation. Polyphosphoric acid (0.168 g) was added, and the pressure was slowly reduced over 40 min to <1 mmHg. The reaction mixture was heated to 285−290 °C for an additional 2 h, during which ethylene glycol was removed by distillation. The progress of the reaction was monitored by current drawn by the mechanical stirrer. The polymer was extruded from the reaction vessel under a positive pressure of nitrogen.

Owing to limited supply of the comonomer **8**, the copolymers containing a large proportion of the 2,6-anthracenedicarboxylate structural unit (4 and 18 mol %: PET-4A and PET-18A, respectively) were prepared on a smaller scale according to the following general procedure. A 50 mL round-bottom flask was charged with dimethyl terephthalate, dimethyl 2,6-anthracenedicarboxylate, **8**, ethylene glycol (7.1 g, 0.12 mol), Mn(CH_3CO_2)$_2$·4H_2O (20 mg, 0.10 mmol), and Sb_2O_3 (40 mg, 0.14 mmol) (Table 1). The flask was fitted with a Claisen still head, an air-cooled condenser, a vacuum adapter, and a round-bottom flask. A thermocouple was inserted into the reaction mixture through a rubber septum on the Claisen adapter, and the system was purged with nitrogen. The flask was heated to 170 °C in a sand bath. A needle was placed through the septum so that it reached the bottom of the flask, and nitrogen was bubbled through the mixture. Transesterification started and methanol began distilling from the reaction. After 1 h at 170 °C, during which methanol distilled from the reaction mixture, the flask was heated to 200 °C for 2 h. The flask was then heated to 280 °C for 15 min, during which time the excess ethylene glycol was distilled. The nitrogen inlet was removed, the rubber septum was replaced with a ground glass thermometer adapter, and the apparatus was evacuated to <0.5 mmHg for 3 h, while the temperature was maintained between 280 and 290 °C. The flask was cooled to room temperature under a flow of nitrogen. The polymer was dissolved in trifluoroacetic acid (100 mL), and the solution was added slowly to methanol (1 L). The precipitated polymer was filtered and dried in a vacuum oven at 90 °C for 12 h.

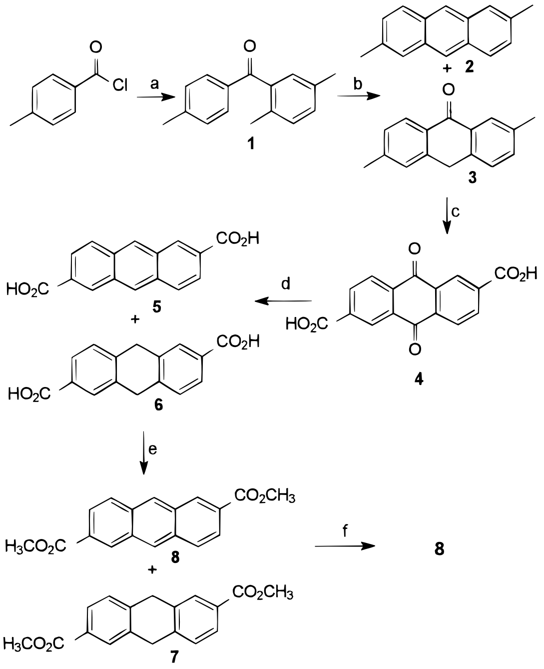


Figure 1. Synthesis of dimethyl 2,6-anthracenedicarboxylate, **8**.

Results and Discussion

Monomer Synthesis. Dimethyl 2,6-anthracenedicarboxylate, **8**, was synthesized in the route outlined in Figure 1. Friedel-Crafts acylation of *p*-toluoyl chloride with *p*-xylene gave 2,5,4′-trimethylbenzophenone, **1**,[25] as a white solid. A 2:3 mixture of 2,6-dimethylan-

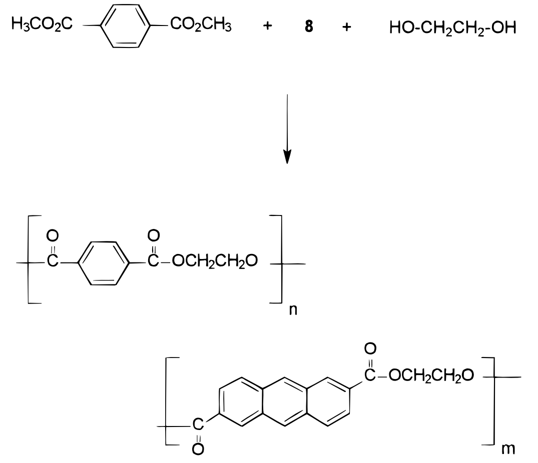
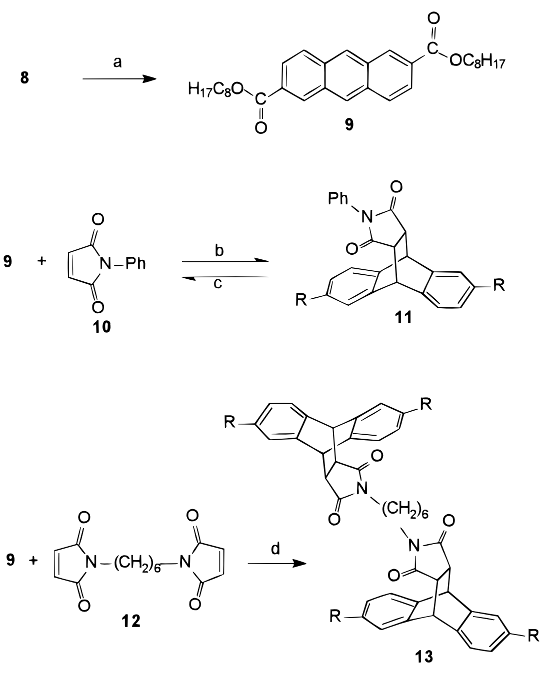


Figure 2. Synthesis of poly(ethylene terephthalate-*co*-2,6-anthracenedicarboxylate), PET−A.

thracene, **2**, and 2,6-dimethyl-9(10*H*)-anthracenone, **3**, was formed upon heating **1** at reflux under air.[25] The crude mixture was oxidized with an excess of chromium trioxide[26] to give 2,6-anthraquinonedicarboxylic acid, **4**, as a yellow solid. **4** was reduced with zinc/cupric sulfate in aqueous ammonium hydroxide at reflux[28] to provide a 1:2 mixture of the desired 2,6-anthracenedicarboxylic acid, **5**, and the over-reduced 9,10-dihydro-2,6-anthracenedicarboxylic acid, **6**. Treatment of the mixture with iodomethane and lithium carbonate in DMF[29] gave the corresponding dimethyl esters: 2,6-dimethyl 9,10-dihydroanthracenedicarboxylate, **7**, and dimethyl 2,6-anthracenedicarboxylate, **8**. This mixture was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to aromatize **7** to give pure **8** as a bright yellow solid.

Polymer Synthesis. Melt polymerization of dimethyl terephthalate, dimethyl 2,6-anthracenedicarboxylate, **8**, and ethylene glycol gave copolymers of PET containing the 2,6-anthracenedicarboxylate structural unit (Figure 2). Three different copolymer compositions were synthesized. The compositions of the polymers 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; C-9,10 and C-1,5 of the anthracene units, respectively) to the singlet at 8.23 ppm (corresponding to the four equivalent aromatic protons of the terephthalate structural unit). The copolymer compositions were in accord with the monomer feed ratio although small discrepancies might be attributed to error in determining the integration of NMR peaks (Table 1).

The polymers were analyzed by DSC to determine the glass transition temperature, T_g, and the melting point, T_m. DSC thermograms of the copolymers demonstrate that they are thermally stable upon cycling from 50 to 300 °C. As shown in Table 1, the copolymer composition effects the thermal properties of the copolymers. Incorporation of 2% of the anthracenedicarboxylate unit into PET increases the T_g and decreases the T_m. (Both samples were prepared by the same method.) Similarly, comparing the two copolymers prepared on a small scale (PET-4A and PET-18A) indicates that addition of more of the anthracene unit further raises the T_g. 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. As shown in Table 1, the percent crystallinity is not affected by the small amounts of anthracenedicarboxylate ($\leq$4%). However, PET-18A does not display a melting endotherm: The high concentration of anthracenedicarboxylate units prevents crystallization.



R = CO$_2$(CH$_2$)$_7$CH$_3$ (a) 1-BuLi, 1-octanol, THF, rt, 24 h; (b) neat, 125 °C,12 h; (c) neat, 250 °C, 7 h; (d) neat, 125 °C, 15 h.

Figure 3. Synthesis ofmodel compounds **9**, **11**, and **13**.

Model Reactions. Model compounds were prepared to determine the conditions for forward and reverse Diels−Alder reactions of anthracenedicarboxylates with maleimides. Dimethyl 2,6-anthracenedicarboxylate, **8**, was converted to the more soluble dioctyl 2,6-anthracenedicarboxylate, **9**, by reaction with lithium octyloxide (Figure 3). A neat mixture of dioctyl 2,6-anthracenedicarboxylate, **9**, and *N*-phenylmaleimide, **10**, was heated at 125 °C for 12 h to give the corresponding Diels−Alder adduct **11**, which was isolated by column chromatography. The ^{1}H NMR spectrum of **11** shows two singlets (8.12 and 8.04 ppm) corresponding to the protons arising from the C-1 and C-5 positions of the adduct (numbered according to the assignment of positions of the original anthracene). These protons are rendered inequivalent by their endo/exo relationship to the imide group. The *N*-phenyl ring of the imide shields one of the protons, thereby shifting the signal upfield. A multiplet at 6.54 ppm is attributed to the protons on C-3 and C-4 that are also shifted upfield by the phenyl group. The two bridgehead protons (C-9 and C-10) of **11** appear as a singlet at 5.04 ppm.

As a model for the cross-linking of polyesters, a mixture of dioctyl 2,6-anthracenedicarboxylate, **9**, and 1,1′-(1,6-hexanediyl)bis(1*H*-pyrrole-2,5-dione), **12**, was heated at 125 °C to afford the corresponding Diels−Alder adduct **13**, which was purified by column chromatography and recrystallization from MeOH/THF (Figure 3). The endo/exo relationship of the arenes to the imide breaks the symmetry present in **9**, thereby rendering the aromatic protons inequivalent. However, in **13**, in contrast to **11**, there is no *N*-phenyl group to cause an upfield shift of the aromatic protons (which all appear at >7.5 ppm).

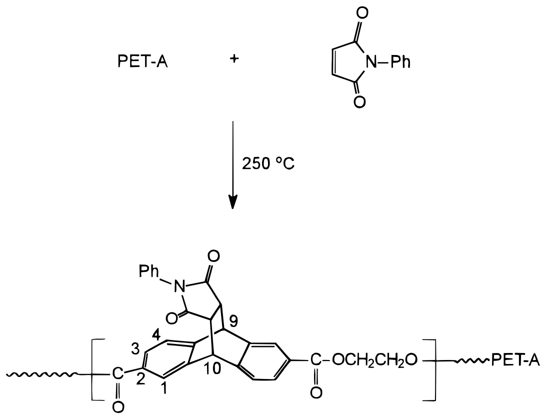


Figure 4. Grafting of *N*-phenylmaleimide, **10**, onto PET−A.

Table 2. Grafting of PET-4A with 10 (Melt Mixing)

time (min)[a]	unreacted anthracene (%)[b]	Diels−Alder adduct (%)[b]	unreacted *N*-phenylmaleimide (%)[b]	extent of reaction (%)[b]
5[c]	2.8	0.8	0.4	23
5[d]	2.2	1.4	0.1	38
10[c]	1.9	2.0	0.2	51

[a] Time at 250 °C. [b] Determined by ^{1}H NMR integration; see Discussion section. [c] Samples allowed to cool to room temperature. [d] Samples remained in the oil bath as it cooled to room temperature.

Grafting onto PET-A. To demonstrate that the anthracene structural units in the PET-A copolymer are available for reaction by cycloaddition with maleimides, PET-18A was treated with *N*-phenylmaleimide, **10** (Figure 4). The copolymer and **10** (1 equiv, based on the amount of 2,6-anthracenedicarboxylate structural unit) were dissolved in trifluoroacetic acid, which was removed under reduced pressure before heating to provide an intimate mixture of the two components. The neat mixture was heated to 125 °C for 12 h, and the ^{1}H NMR was recorded in TFA/$CDCl_3$. Comparison of the ^{1}H NMR signals for the adduct (6.54 ppm, m, C-3,4) and the unreacted anthracene (9.0 ppm, s, C-9,10) revealed that 94% of the anthracene groups had undergone Diels−Alder reaction with the maleimide.

The two components (PET-A and *N*-phenylmaleimide, 1 equiv) were also mixed together in the melt. PET-4A and **10** were heated at 250 °C under nitrogen for either 5 or 10 min. ^{1}H NMR spectroscopy (TFA/$CDCl_3$) was used to determine the extent of reaction. As shown in Table 2, the extent of reaction between the anthracene units of the polymer and **10** increases as the time that the reaction mixture is held at high temperature increases.

Cross-Linking of PET-A. To investigate cross-linking, PET−anthracene copolymers were mixed with 0.3 equiv of the bis(dienophile) 1,1′-(1,6-hexanediyl)bis-(1*H*-pyrrole-2,5-dione), **12**, in 1,1,1,3,3,3-hexafluoro-2-propanol, and the solvent was removed under reduced pressure using a rotary evaporator. Separate experiments (DSC) show that the freshly prepared mixtures of PET−A and maleimides are inhomogeneous. The neat mixture was heated at 125 °C. Copolymers PET−4A and PET−18A were rendered insoluble by this treatment (they swelled in TFA without dissolving), suggesting that they are cross-linked by the bis(maleimide) (Figure 5).

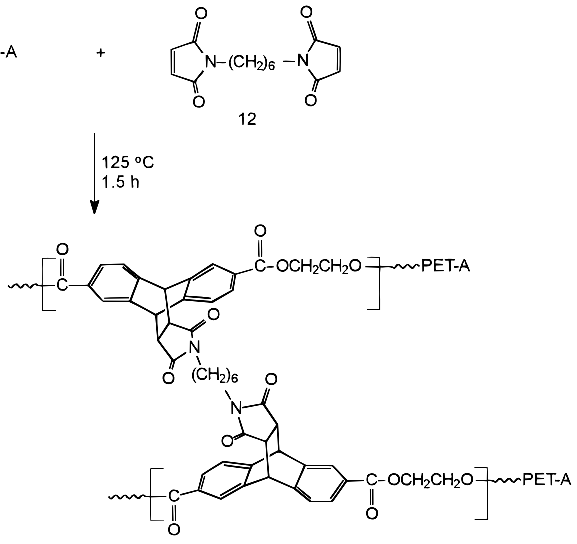


Figure 5. Cross-linking of PET−A with bis(maleimide) **12**.

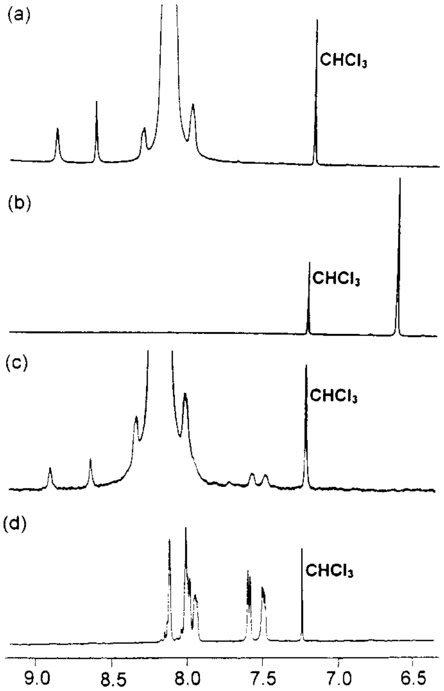


Figure 6. ^{1}H NMR spectra (500 MHz): (a) PET−2A (b) **12**, (c) PET−2A and 0.5 equiv of **12** at 125 °C, (d) **13**. Spectra were obtained using solutions of polymer in $CDCl_3$/TFA (3:1).

PET−2A remained soluble after treatment with the bis(maleimide) under the same conditions, and the ^{1}H NMR spectrum was recorded in TFA/$CDCl_3$. NMR signals of this material corresponded to signals from model compound **13**, thus providing strong evidence that the Diels−Alder reaction is responsible for cross-linking. This evidence is illustrated by the four spectra shown in Figure 6. Figure 6a shows two singlets in the aromatic region of the ^{1}H NMR spectrum of PET−2A at 8.97 and 8.71 ppm. These signals correspond to the protons on C-9,10 and C-1,5 protons of the 2,6-disubstituted anthracene unit. Another singlet at 8.23 ppm corresponds to the four equivalent terephthalate aromatic protons. In Figure 6b, the singlet at 6.70 ppm is assigned to the two vinylic protons of **12**. Figure 6c shows the signals that appear when PET−2A is mixed with 0.5 equiv of **12** at 125 °C. The doublet at 7.54 ppm corresponds to the four protons on C-3,4 of the Diels−Alder adduct of the polymer. This signal correlates with the signal from the model compound **13** shown in Figure

Table 3. Cross-Linking of PET−4A with 12

mol equiv of **12**[a]	temp, °C	time, h	[η], dL/g	M_v,[b] g/mol ($\times 10^3$)
0	125	1.5	0.54 ± 0.01	9.9
0.01	125	1.5	0.75 ± 0.03	15
0.02	125	1.5	0.98 ± 0.01	22
0.03	125	1.5	*c*	*c*
0.50	125	1.5	*c*	*c*
0.01	25	1.5	0.55 ± 0.01	10
0.01	60	1.5	0.55 ± 0.01	10

[a] One mole equivalent of **12** corresponds to 1 mol of anthracenedicarboxylate units. [b] Calculated using Mark−Houwink constants: $K = 6.56 \times 10^{-4}$ dL/g and $a = 0.73$ (ref 23). [c] Insoluble in 2-chlorophenol.

6d. The other signals for the Diels−Alder adduct lie under the signal for the terephthalate protons at 8.23 ppm. The lack of a singlet at 6.70 ppm in Figure 6c indicates that there are no unreacted vinyl groups present, and the reaction has gone to completion.

Dilute solution viscometry was used to investigate the effect of the bis(maleimide) **12** on the molecular weight of PET−4A prior to gelation. PET−4A and small amounts of **12** (0.01−0.5 equiv) were heated at 125 °C for 1.5 h. Viscosity measurements were conducted on ~1.5 wt % solutions of polymers 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.[21] The single point viscometry of PET−4A of 0.54 dL/g corresponds to a molecular weight (M_v) of 9.9×10^3 g/mol (using Mark−Houwink constants of $K = 6.56 \times 10^{-4}$ dL/g and $a = 0.73$).[22] The viscosity increases to 0.75 dL/g (i.e., $M_v = 15 \times 10^3$ g/mol) upon treatment of the copolymer with 0.01 equiv of bis(maleimide) **12** and to 0.98 dL/g (i.e., $M_v = 22 \times 10^3$ g/mol) using 0.02 equiv (Table 3). The increases in molecular weight are higher than expected on the basis of the stoichiometry of the Diels−Alder reaction. This disparity might occur due to errors in the use of single point intrinsic viscosity measurements, the inhomogeneity of the cross-linking reaction mixture (giving regions with higher local concentrations of cross-links), the use of Mark−Houwink parameters for linear PET to estimate the molecular weight of a branched polymer, the fact that M_v is not a direct measure of M_w, and the fact that M_w increases faster than M_n. These data should be treated as qualitative and demonstrate that the molecular weights of the polymers increase with the addition of small amounts of bis(maleimide). The polymer gels and does not completely dissolve in 2-chlorophenol when the copolymer is treated with greater than 0.02 equiv of bis(maleimide).

A mixture of PET−4A and 0.01 equiv of bis(maleimide) was held at various temperatures for 1.5 h to determine the effect of temperature on the increase in molecular weight of polymers as a consequence of Diels−Alder reactions. The intrinsic viscosity and ^{1}H NMR spectra of copolymers treated with bis(maleimide) at room temperature and 60 °C indicate that the Diels−Alder reaction does not occur at these temperatures in the allotted time.

Thermal Analysis of Bis(maleimide)-Treated Copolymers. PET−4A ($T_m = 236$ °C), treated with 0.5 equiv of bis(maleimide) at 125 °C, gives a melting point of 205 °C, indicating that formation of cross-links disrupts crystallinity (Figure 7). The enthalpy of melting for this sample ($\Delta H_m = 34.47$ J/g) corresponds to 28% crystallinity. This higher degree of crystallinity compared to the starting polymer results from annealing of the samples during the cross-linking reaction at 125 °C. No crystallization exotherm appears upon cooling the bis(maleimide)-treated polymer 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 primarily in the amorphous regions of the polymer. The effect of cross-links on the crystalline phase is only observed after heating to the isotropic melt. As shown in Figure 8, treatment of PET−4A with smaller amounts of bis(maleimide) (0.02 equiv) impedes crystallization to a smaller extent. The melting transition is present during the first heating curve and decreases in the second and third heating curves.

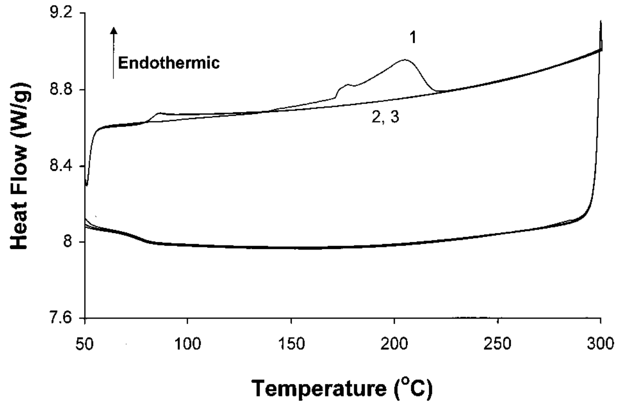


Figure 7. DSC thermogram of PET−4A cross-linked with 0.5 equiv of **12**; see Experimental Section. Heating rate = 10 °C/min. Three heating−cooling cycles are shown.

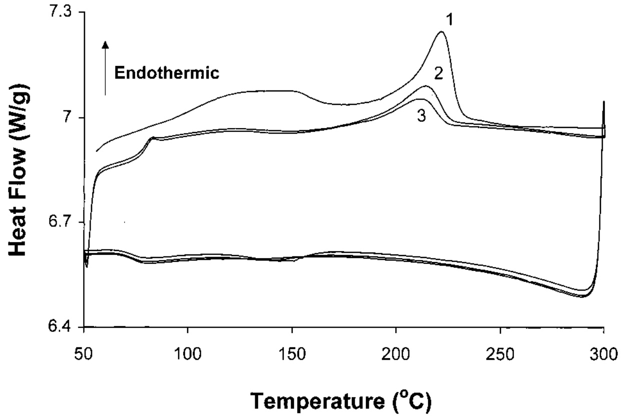


Figure 8. DSC thermogram of PET−4A cross-linked with 0.03 equiv of **12**; see Experimental Section. Heating rate = 10 °C/min. Three heating−cooling cycles are shown.

Reversible Cross-Linking. The Diels−Alder reaction between dioctyl 2,6-anthracenedicarboxylate, **9**, and *N*-phenylmaleimide, **10**, to give the Diels−Alder adduct (Figure 3) is partially reversible upon heating at 250 °C. The extent of reaction was determined by comparison of the ^{1}H NMR spectrum of the reaction mixture with that of **9**. Singlets at 8.81 and 8.59 ppm corresponding to two protons each for C-9,10 and C-1,5 for **9** increased in intensity, and the multiplet 6.54 ppm corresponding to the two protons on C-3,4 of **11** decreased in intensity. The reverse reaction is approximately 27% complete after heating **11** at 250 °C for 7 h.

To investigate the reversibility of the cross-linking of anthracene-containing copolymers, PET-2A was mixed with 0.5 equiv of 1,1′-(1,6-hexanediyl)bis(1*H*-pyrrole-2,5-dione), **12**, and heated at 125 °C. ^{1}H NMR spectroscopy of the bis(maleimide)-treated PET-2A showed a doublet at 7.54 ppm corresponding to the four protons on C-3,4 of the Diels−Alder adduct of the polymer. The cross-linked polymer was then heated at 250 °C for 15 h. ^{1}H NMR spectroscopy of the resulting material did not show a change in the intensity of the doublet at 7.54 ppm of the polymeric Diels−Alder adduct relative to the two singlets for the protons on C-9,10 and C-1,5 of the unreacted anthracene subunits. This indicates that the reverse Diels−Alder reaction does not occur in this cross-linked polymer.

Conclusions. We have demonstrated the grafting, chain extension, and cross-linking of anthracene-containing copolymers of PET by Diels−Alder cycloaddition with low molecular weight maleimides. The Diels−Alder reaction of low molecular weight anthracenes and maleimides is reversible, but studies on model compounds show the reverse reaction occurs only slowly at 250 °C. Since the PET−anthracene copolymers are prone to thermal decomposition at such high temperatures over extended periods, development of practical reversible cross-links in PET requires careful consideration of the kinetics and temperature profiles for the forward and reverse Diels−Alder reactions.[21] This work also suggests a route to grafting dienophiles or dienophile-substituted polymers to improve the properties of PET.

Acknowledgment. We thank KoSa (formerly Hoechst Celanese/Trevira Corp.) for support of this research. D.M.C. gratefully acknowledges the support of the National Science Foundation in the form of a CAREER award.

References and Notes

(1) *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1985; Vol. 7, p 551.
(2) *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1985; Vol. 12, p 52.
(3) Bikiaris, D.; Karayannidis, G. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1705.
(4) Borman, W. U.S. Patent 3953404, 1976.
(5) Loontjens, T.; Belt, W.; Stanssens, D.; Weerts, P. *Makromol. Chem., Macromol. Symp.* **1993**, *75*, 211.
(6) Inata, H.; Matsumura, S. *J. Appl. Polym. Sci.* **1986**, *32*, 4581.
(7) Akkapeddi, M.; Gervasi, J. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1988**, *29*, 567.
(8) Li, C.-H.; Hsu, K.-Y.; Chang, T.-C. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 1119. Ikeda, T.; Itakura, H.; Lee, C.; Winnik, F. M.; Tazuke, S. *Macromolecules* **1988**, *21*, 3536. Vargas, M.; Collard, D.; Liotta, C.; Schiraldi, D., unpublished results.
(9) Inata, H.; Morinaga, T.; Matsumura, S. *J. Appl. Polym. Sci.* **1988**, *35*, 1705.
(10) Kriegel, R.; Collard, D.; Liotta, C.; Schiraldi, D. *Macromolecules* **1998**, *31*, 2475.
(11) Sijbesma, R.; Beijer, F.; Brunsveld, L.; Folmer, B.; Hirschberg, J.; Lange, R.; Lowe, J.; Meijer, E. *Science* **1997**, *278*, 1601.
(12) Feng, D.; Wilkes, G. *Macromolecules* **1991**, *24*, 6788.
(13) Zimmerman, R.; Dennis, K.; Moore, E. U.S. Patent 3,678,016, 1972.
(14) Pazos, J. U.S. Patent 3,872,057, 1975.
(15) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415.
(16) Stille, J.; Plummer, L. *J. Org. Chem.* **1961**, *26*, 6.
(17) Kuramoto, N.; Hayashi, K.; Nagai, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2501.
(18) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1990**, *23*, 2636.
(19) Craven, J. U.S. Patent 3,435,003, 1966.
(20) Bell, V.; Havens, S. U.S. Patent 4,661,55, 1987.
(21) Chung, Y.; Duerr, B.; McKelvey, T.; Nanjappan, P.; Czarnik, A. *J. Org Chem.* **1989**, *54*, 1018.
(22) Inata, H. Japanese Patent #745545, Nov 1st 1973, to Teijin, Inc.
(23) Solomon, O.; Ciuta, J. *J. Appl. Polym. Sci.* **1962**, *6*, 683.
(24) Marshall, J.; Todd, A. *Trans. Faraday Soc.* **1953**, *49*, 67.
(25) Morgan, G.; Coulson, E. *J. Chem. Soc.* **1929**, 2203.
(26) Seer, *Monatsch. Chem.* **1911**, *32*, 153.
(27) Kravtsov, V.; Moshchinskaya, N.; Kochneva, E.; Kolodyazhnyi, O. *Khim. Tekhnol., Respub. Mezhvedom. Nauch.-Tekh. Sb.* **1966**, 6, 155. Chem. Abstr. 68, 87053v, 1968.
(28) Broene, R. D.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 5227.
(29) Staab, H.; Sauer, M. *Liebigs Ann. Chem.* **1984**, 742.
(30) Meth-Cohn, O. *J. Chem. Soc., Chem. Commun.* **1986**, 695.
(31) Searle, N. U.S. Patent 2,444,536, 1948.
(32) Braun, D.; Cherdron, H.; Kern, W. *Techniques of Polymer Synthesis and Characterization;* John Wiley & Sons: New York, 1972; p 208.

MA990638Z