

## A New Reaction of Bisphenol A and Preparation of Polysubstituted 9,9-Dimethylxanthenes<sup>†</sup>

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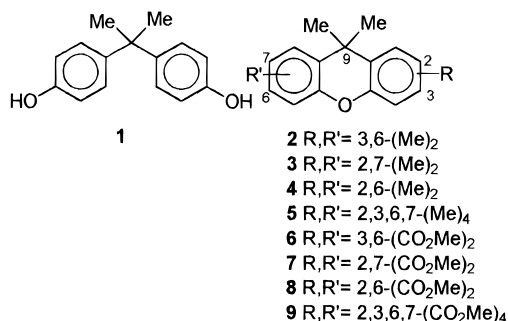
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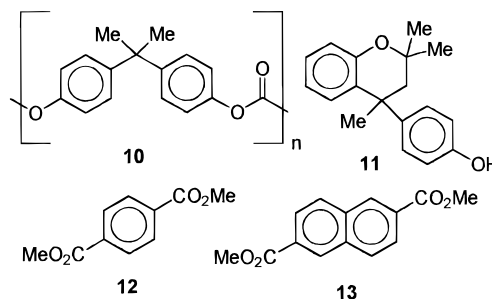
A new transformation of bisphenol A (**1**) to polymethylated 9,9-dimethylxanthenes **2–5** in the presence of an exogenous phenol is described. The reaction proceeds with concurrent liberation of phenol, is catalyzed by strong acid, and takes place at synthetically useful rates at temperatures above 100 °C. Materials chemically related to bisphenol A, polycarbonate **10**, chroman **11**, and tars generated during the manufacture of **1**, behave similarly. The product xanthenes are useful as precursors to novel xanthene polyesters such as **33** having high glass transition temperatures relative to analogous materials based on **12** or **13**. Catalytic oxidation of xanthenes **2–4** affords highly insoluble diacids that are esterified to the esters **6–8**. A mechanistic framework accounting for the appearance of chroman **23** and spiroketal **24** as intermediates is given. Overall, the reaction has the characteristics of a complex series of equilibria in which xanthenes such as **2** are strongly favored.

In this paper, we describe a useful new transformation of bisphenol A (**1**) into polymethylated 9,9-dimethylxanthenes **2–5**. The transformation is generally ap-

tion temperatures relative to analogous polyesters based on dimethyl terephthalate (**12**) or dimethyl naphthalene-2,6-dicarboxylate (**13**).<sup>4</sup> Apart from the general felicity



plicable to **1** and chemically related materials exemplified by BPA polycarbonate **10**, chroman **11**, and acetone, each of which may serve as the source of the isopropylidene group of the product xanthenes. Exposure of **1** to excess *m*- or *p*-cresol or 3,4-dimethylphenol (3,4-DMP) and methanesulfonic acid (MSA) at moderate temperature affords one of the aforementioned xanthenes in good yield and a nearly quantitative yield of liberated phenol. Mechanistic details of this transformation and experiments illustrating its generality and utility are presented here. Although xanthene **2** was first described in 1968 by Ourisson,<sup>1</sup> direct synthetic approaches to polymethylated xanthenes were lacking until recently.<sup>2</sup> We show here that polymethylated xanthenes are readily converted to the xanthenedi- and tetracarboxylates **6–9**.<sup>3</sup> The xanthene dicarboxylates **6–8** have proven useful as precursors to novel polyesters having high glass transi-



attendant upon the appearance of a new synthetic tool, the method described here also represents a potential environmental advance in that it provides a single, benign outlet for starting materials, byproducts, and post-consumer debris generated during the manufacture and use of polycarbonate **10**.

One of the principal characteristics of bisphenol A (**1**) is its tendency to undergo acid- or base-catalyzed fragmentation to phenol (**14**) and 4-isopropenylphenol (**15a**). This mode of reactivity has been used to prepare 4-isopropenylphenol itself<sup>5</sup> or substituted 4-isopropenylphenols.<sup>6</sup>

In its *p*-quinone methide tautomeric form **15b**, 4-isopropenylphenol is subject to reaction with a variety of nucleophiles, including hydride,<sup>7</sup> cyanide,<sup>8</sup> aniline,<sup>9</sup> or

(3) Xanthene-4,5-dicarboxylates bearing pendant alkyl groups form the structural basis of synthetic replicators, molecular compliments to imides and molecular clefts. Nowick, J. S.; Ballester, P.; Ebmeyer, F.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 8902. Park, T. K.; Schroeder, J.; Rebek, J., Jr. *Ibid.* **1991**, *113*, 5125. Park, T. K.; Feng, Q.; Rebek, J., Jr. *Ibid.* **1992**, *114*, 4529.

(4) Caruso, A. J.; Lee, J. L. US Patent 5,466,777, Nov 14, 1995; 5,504,184, Apr 2, 1996.

(5) Corson, B. B.; Heintzelman, W. J.; Schwartzman, L. H.; Tiefenthal, H. E.; Lokken, R. J.; Nickels, J. E.; Atwood, G. R.; Pavlik, F. J. *J. Org. Chem.* **1958**, *23*, 544. Inoue, K. US Patent 4,594,459, Jun 10, 1986. Nagayo, T.; Otsubo, T.; Kuno, S.; Iimuro, S. JP 62,148,441, Jul 2, 1987; *Chem. Abstr.* **1988**, *109*, 149054x. Crivello, J. V.; Ramdas, A. *J. Mater. Sci. Pure Appl. Chem.* **1991**, *113*, A29(9), 753.

(6) Tashiro, M.; Watanabe, H.; Oe, K. *Org. Prep. Proced. Int.* **1975**, *7*, 189.

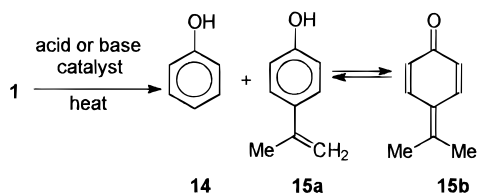
(7) Olah, G. A.; Kaspi, J.; Meidar, D. *Synthesis* **1978**, 396.

<sup>†</sup> This paper is dedicated to Professor Nikolaus H. Fischer.

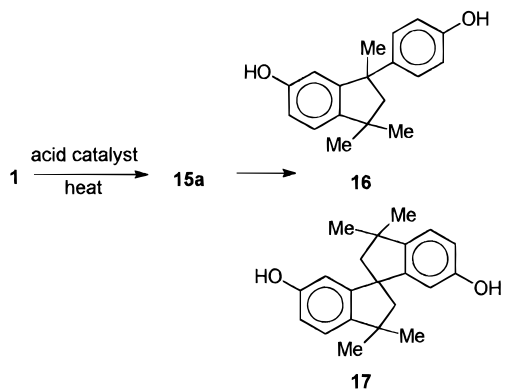
<sup>Ⓞ</sup> Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Xanthene **2** was produced as a minor byproduct in the condensation of pulegone with orcinol followed by dehydrogenation–hydrogenolysis of the intermediate 1-hydroxy-3,6,9,9-tetramethyl-5,6,7,8-tetrahydroxanthene<sup>1a</sup> or in a phosphorus oxychloride-mediated condensation reaction between *m*-cresol and acetone, which gave **2** in 2.5% yield.<sup>1b</sup> (a) Ourisson, G.; Chazan, J. B. *Bull. Soc. Chim. Fr.* **1968**, 1374. (b) *Ibid.* **1968**, 1384.

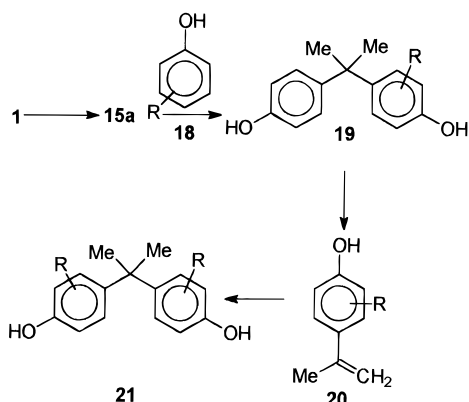
(2) Xanthene dianhydrides related to **9** show promise as components of nearly rodlike polyimides. Trofimenko, S. US Patent 5,051,520, Sept 24, 1991. Auman, B. C.; Trofimenko, S. *Macromolecules* **1994**, *27*, 1136.



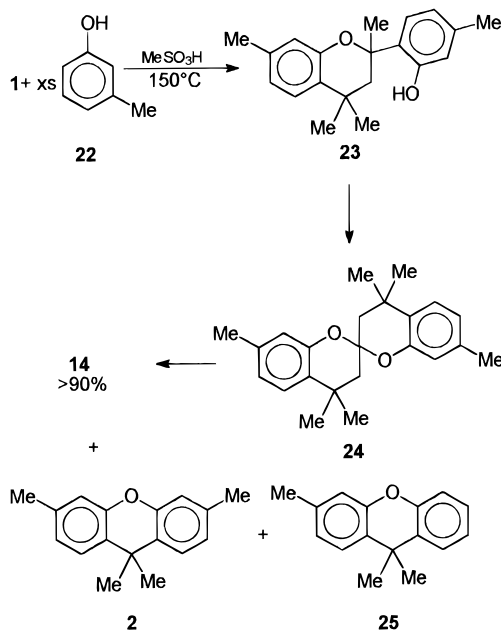
another phenol.<sup>10</sup> Upon heating under neutral conditions, **15a** dimerizes in an apparent ene reaction and undergoes linear trimerization under selected acidic conditions.<sup>11</sup> Upon vigorous treatment with acid neat **1** has been shown to afford indan dimer **16** and spiroindan bisphenol **17** in high yield, presumably via the intermediate **15a**.<sup>12</sup>



Given its proclivity to fragmentation to **15a**, we were confident that novel bisphenols **21** could be prepared from **1** upon acid treatment in the presence of excess substituted phenol. As had been demonstrated earlier by Mark,<sup>10a</sup> capture of **15a** by an exogenous phenol **18** gives first a mixed bisphenol **19**. A further cycle of fragmentation and capture affords a new bisphenol **21** via the substituted isopropenylphenol **20**. We anticipated that materials containing embedded BPA moieties such as polycarbonate **10** or other phenol–acetone condensation products,<sup>13</sup> isomeric bisphenols, trisphenols, and chromans, generated as byproducts in the manufacture of **1** might behave similarly.



Initially, we observed that **1** upon treatment with excess *m*-cresol, **22**, containing methanesulfonic acid, was rapidly transformed at 150 °C into a suite of high-boiling products and a nearly quantitative yield of liberated phenol.



Over the course of several hours, the mixture of products was transformed into a single major, high-boiling component that was found to be 3,6,9,9-tetramethylxanthene (**2**).<sup>1</sup> We found no evidence for the formation of spirobiindan **17**.<sup>14</sup> When carried out on a 50 g scale, **1** was converted cleanly to crude xanthene **2** as a distillable, waxy, off-white solid in 72% yield. The primary contaminant was 3,9,9-trimethylxanthene (**25**). Two of the initially formed products in this reaction were identified by GCMS and assigned structures **23** and **24**, respectively. Chroman **23** was prepared independently<sup>15</sup> by condensation of acetone with *m*-cresol in the presence of HCl. Spiroketal **24**<sup>16</sup> was obtained from the initial product mixture by column chromatography. When resubjected to the reaction conditions, each of compounds **23** and **24** afforded tetramethylxanthene **2** in high yield. A kinetic profile for the reaction of **1** with *m*-cresol and MSA is given in Figure 1 below. It illustrates the intermediacy of compounds **23** and **24** and three other intermediates (labeled unknowns 1–3).

A mechanistic framework that accounts for both the formation of xanthene derivative **2** from BPA through the intermediacy of chroman **23** and spiroketal **24** is given below. Bisphenol A fragments to **15a**, the isopropenyl group of which is transferred efficiently to the *m*-cresol solvent to give **27a**<sup>17</sup> via the mixed bisphenol **26**. Capture of **27a** by excess *m*-cresol gives the *o,o*-bisphenol **28**, which undergoes acid-catalyzed dehydration to give product 3,6,9,9-tetramethylxanthene (**2**). The

(10) (a) *o*-Cresol, 2,6-dimethylphenol, *p*-cresol, 2,3,6-trimethylphenol, and 2,6-dichlorophenol: Mark, V.; Hedges, C. V. US Patent 4,560,808, Dec 24, 1985. (b) Catechol: Tomioka, A.; Nakanishi, H.; Kuwana, K.; Kamiya, Y.; Hanabatake, M.; Oi, S. JP 02,172,936, Dec 26, 1988; *Chem. Abstr.* **1990**, 113, 221391g. (c) 2,6-Diphenylphenol: Wang, Z. Y.; Hay, A. S. *Synthesis* **1989**, 471. (d) Resorcinol: Ito, M.; Iimuro, S. JP 04,364,147, Oct 8, 1990; *Chem. Abstr.* **1993**, 118, 233643g.

(11) Farnham, A. G. US Patent 3,288,864, Nov 29, 1966. (12) Curtis, R. F. *J. Chem. Soc.* **1962**, 415. Krimm, H.; Buysch, H. J. Ger. Offen. 2,645,020, Apr 13, 1978; *Chem. Abstr.* **1978**, 89, 24036e. Faler, G. R.; Lynch, J. C. US Patent 4,701,566, Oct 20, 1987.

(13) Neumann, F. W.; Smith, W. E. *J. Org. Chem.* **1966**, 31, 4318. (14) Spirobiindan **17** was found to be stable under the reaction conditions.

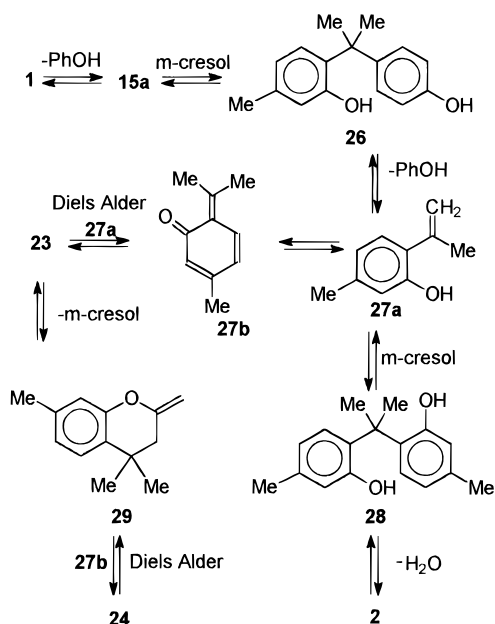
(15) Baker, W.; Besly, D. M. *J. Chem. Soc.* **1940**, 1103. (16) Baker, W.; Besly, D. M. *J. Chem. Soc.* **1939**, 195. Baker, W.; McOmie, J. F. W.; Wild, J. H. *Ibid.* **1957**, 3060.

(17) Divakar, K. J.; Rao, A. S. *Synth. Commun.* **1976**, 6, 423.

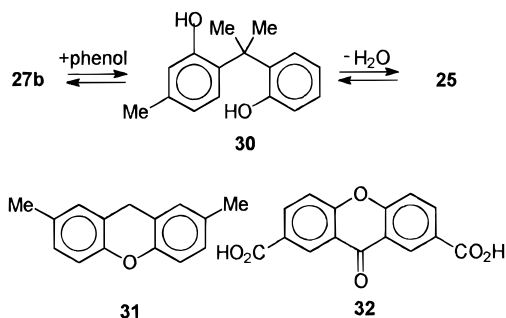
(8) Morgan, T. A. US Patent 4,806,673, Feb 21, 1989.

(9) Krimm, H.; Ruppert, H.; Schnell, H. US Patent 3,418,371, Dec 24, 1968. Hefner, R. E., Jr. US Patent 4,683,276, Jul 28, 1987.

appearance of chroman **23** and spiroketal **24** as intermediates is consistent with a complex series of equilibria in which tetramethylxanthene **2** is strongly favored. Chroman **23** is thought to be the product of a Diels–Alder reaction of **27a** with its tautomer **27b**. Loss of *m*-cresol from **23** affords the presumed intermediate, chromene **29**, which suffers a second Diels–Alder reaction with **27b** to give spiroketal **24**.



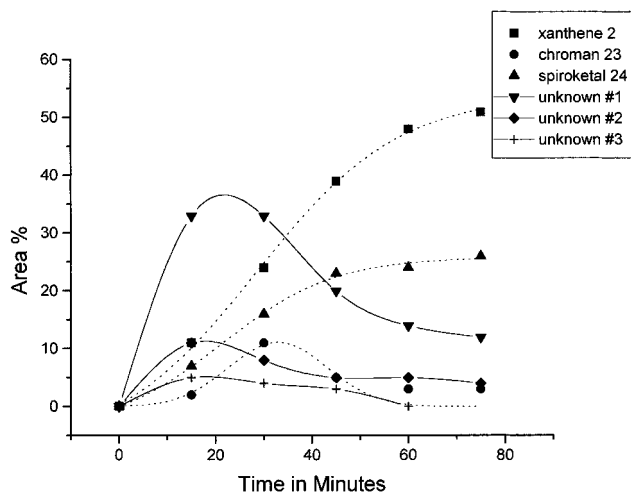
A significant side reaction in xanthene formation from bisphenol A involves capture of 2-isopropenyl-5-methylphenol (**27a**) by phenol to give the *o,o*-bisphenol **30**, which upon dehydration affords the known<sup>1</sup> trimethylated product **25**.



An attempt at continuous removal of phenol from the reaction mixture during the preparation of tetramethylxanthene **3** from **1** and *p*-cresol led to the formation of the known unsubstituted xanthene **31**<sup>18</sup> (mp 165–167 °C (lit.<sup>18</sup> mp 165 °C)) as a major byproduct whose structure was confirmed by its transformation to xanthone diacid **32**.<sup>19</sup> Compound **31** appears to result from oxidation of *p*-cresol followed by methylene group transfer to excess *p*-cresol and dehydration under the reaction conditions. The formation of trimethylxanthenes such as **25** could be suppressed using more dilute reaction conditions. Typically, we used 1.0 L of *m*-cresol per 50 g of BPA employed. Under these conditions, we obtained product polymethylated xanthenes **2** and **25** in a ratio of about

(18) Reilly, J.; Drumm, P. J.; Barrett, H. S. B. *J. Chem. Soc.* **1927**, 67.

(19) Pfeifer, J.; Duthaler, R. US Patent 4,714,669, Dec 22, 1987.



**Figure 1.** Kinetic profile of the reaction of BPA with *m*-cresol containing methanesulfonic acid at 150 °C.

**Table 1.** Conversion of BPA to Xanthenes 2–5. Substrates, Catalyst Loading, Reaction Conditions, Products, and Product Yields

entry	RPhOH	mole ratio BPA/cat.	<i>T</i> (°C)	time (h)	yield phenol (%)	product	product yield(s) (%)
1	<i>m</i> -cresol	29	125	17	79	<b>2</b>	12.5
2	<i>m</i> -cresol	1.1	150	1	95	<b>2</b>	42
3	<i>m</i> -cresol	1.1	150	3	96	<b>2</b>	60.4
4	<i>m</i> -cresol	1.1	150	23	92	<b>2</b>	79.5
5	<i>m</i> -cresol	55 <sup>a</sup>	145	17	81	<b>2</b>	2
6	<i>m</i> -cresol	1.1	150	50	95	<b>2</b>	72
7	<i>m</i> -cresol	No Cat.	150	41	0	<b>2</b>	0 <sup>b</sup>
8	<i>m</i> -cresol	2.2	100	71.5	92	<b>2</b>	57
9	<i>p</i> -cresol	2.2	150	15	100	<b>3</b>	48
10	3,4-DMP	2.1	100	40		<i>c</i>	57 <sup>d</sup>
11	3,4-DMP	2.1	100	71	100	<b>5</b>	<i>c</i>
12	2,4-DMP	3.1	150	12	68		0
13	<i>m,p</i> -cresol (1:1)	3.9	135	45	90	<b>2, 3, 4</b> <sup>e</sup>	62
14	<i>o</i> -cresol	2.0	140	52	96		0

<sup>a</sup> Catalyst was Nafion fluorinated sulfonic acid resin. Otherwise, the catalyst was CH<sub>3</sub>SO<sub>3</sub>H. <sup>b</sup> In the absence of catalyst recovery of BPA was quantitative. <sup>c</sup> Yield of product (phenol or xanthene) was substantial but was not made quantitative. <sup>d</sup> Yield of crude product. <sup>e</sup> As a 1.9:1:4.8 mixture of tetramethylxanthenes **2**, **3**, and **4**.

10–12:1. Excess *m*-cresol can be recovered by distillation and reused. Liberated phenol may be recovered from the *m*-cresol using a known extractive distillation procedure.<sup>20</sup>

In range-finding studies various alkylated phenols, catalyst loadings, reaction times, and temperatures were examined. Substrates, reaction conditions, products, and yields are gathered in Table 1. Xanthene formation works well for both *m*- and *p*-cresol as well as 3,4-dimethylphenol, which afford tetramethylxanthenes **2** and **3** and hexamethylxanthene **5**, respectively. Best yields of 3,6,9,9-tetramethylxanthene (**2**) are obtained at 150 °C when substantial amounts of methanesulfonic acid catalyst are used and as the reaction time approaches 24 h (Table 1, entries 1–4). The reaction does not occur in the absence of a catalyst, in which case BPA is recovered unchanged (Table 1, entry 7). BPA itself is highly sensitive to other acidic catalysts under these conditions (Table 1, entry 5). In all cases, the trimethylated product **25** or its equivalent was present as a

(20) Wust, A.; Hammerstroem, K. US Patent 4,325,789, Apr 20, 1982.

significant (5–10%) impurity in the product xanthene. The reaction fails unaccountably when either 2,4-dimethylphenol or *o*-cresol is employed (Table 1, entries 12 and 14). Although **1** is converted quantitatively to phenol in the presence of acid and excess *o*-cresol little or no polymethylated xanthene product is observed (Table 1, entry 14).

A tetramethylxanthene **4** having its benzylic methyl groups arrayed along the "long axis" of the molecule may be obtained as the principle component in a mixture with xanthenes **2** and **3** by reaction of BPA with a 1:1 mixture of *m*- and *p*-cresol (Table 1, entry 13).

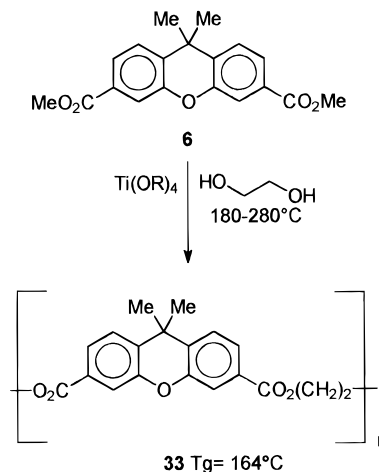
The conversion of bisphenol A to polymethylated xanthenes with liberation of phenol holds potential for recovery of material values from debris generated in the manufacture of bisphenol A polycarbonate. For example, mixtures of condensation products of phenol with acetone (BPA tars)<sup>21</sup> consisting primarily of mixtures of bisphenol A (**1**) with its *o,p*-isomer and chroman **11** are converted to substantially pure tetramethylxanthene **2** with concomitant liberation of phenol (see the Experimental Section).<sup>22</sup> Pure chroman **11** is also converted to xanthene **2** and phenol though somewhat less efficiently than BPA under typical reaction conditions. We have found as well that a variety of BPA polycarbonate-containing materials can serve as latent sources of BPA for the xanthene-forming reaction, and an example of this process is given in the Experimental Section.

Although one can envision a host of uses for polymethylated 9,9-dimethyl xanthenes **2–5**, compounds that are stable at high temperature and have an agreeable odor relative to the malodorous parent 9,9-dimethylxanthene,<sup>23</sup> we focused on their utility as precursors to the corresponding dicarboxylic acids for use in polymer synthesis. Benzylic oxidation of tetramethylxanthenes **2–4** using a variant of the Mid-Century process<sup>24</sup> followed by Fischer esterification afforded new 9,9-dimethylxanthene dicarboxylic esters **6–8**. Efforts to oxidize hexamethylxanthene **5** catalytically were hampered by the complexity of the product mixtures obtained. Tetraester **9** was obtained upon treatment of hexamethylxanthene **5** with a stoichiometric amount of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water at 250 °C under autogenous pressure of 595 psi followed by esterification.<sup>25</sup>

The di- and tetraacid intermediates are highly insoluble and are conveniently isolated in pure form from the reaction mixture by filtration. In the case of tetramethylxanthene **4**, obtained initially as a 2:1:4.7 mixture of xanthenes **2**, **3**, and **4**, respectively, catalytic oxidation affords the corresponding mixture of diacids. The insolubility of the diacids plays an important role in the removal of undesired monoacids derived from trimethylated products such as **25**, which are found in all xanthenes prepared from BPA or a BPA-like material capable of releasing phenol under acidic conditions.

The esters **6–9** are soluble and are readily converted into novel polyesters<sup>4</sup> using standard melt polymerization techniques. The preparation and properties of these new

materials will be described in detail elsewhere.<sup>26</sup> For the present, we note that xanthene polyesters based on diesters **6–8** range from amorphous to crystalline materials and show significantly higher glass transition temperatures than the corresponding dimethyl terephthalate **12** or naphthalene-2,6-dicarboxylate **13**-based polymers. Thus, poly(ethylenexanthene-3,6-dioate) (**33**) gave a tough transparent film when molded on a Carver press, was amorphous, and displayed a glass transition temperature of 164 °C.<sup>27</sup>



In conclusion, a new and useful reaction of bisphenol A (**1**) with substituted phenols in the presence of methanesulfonic acid has been evaluated. The method allows the efficient large-scale preparation of product polymethylated 9,9-dimethylxanthenes, which we have shown to be readily converted to xanthene di- and tetracarboxylic esters. The diesters can be converted to novel polyesters having markedly higher glass transition temperatures than analogous materials based upon conventional diesters **12** and **13**. The synthetic methodology developed offers a unique opportunity to create potentially useful new materials such as polyester **33** from waste materials generated during the manufacture and use of BPA polycarbonate **10**.

## Experimental Section

**General Methods.** Melting points are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR were measured in CDCl<sub>3</sub> on a GE-QE 300 instrument unless otherwise indicated. Chemical shifts are reported in ppm relative to tetramethylsilane (0 ppm). Reaction progress was followed by GC and/or TLC. In nonpreparative experiments, yields were determined by GC using an internal standard, biphenyl or tetradecane, together with an independently derived calibration table. Small-scale reactions were carried out in 20 mL screw cap vials equipped with magnetic fleas. Bisphenol A tar and chroman **11** starting materials were obtained from GE Plastics, Mt. Vernon, IN. Glass transition temperatures (*T*<sub>g</sub>'s) and some melting points were determined by differential scanning calorimetry (DSC).

**Preparation of 3,6,9,9-Tetramethylxanthene (2).**<sup>1</sup> **General Method.** The following procedure is generally applicable to the preparation of xanthenes **2–5** from bisphenol **1**, polycarbonate **10**, chromans **11** and **23**, spiroketal **24**, BPA tars, and acetone. Following the progress of the reaction by GC is recommended in order to assure complete conversion of

(21) Carnahan, J. C. US Patent 4,277,628, Jul 7, 1981.

(22) Caruso, A. J.; Lee, J. L. US Patent 5,430,199, Jul 4, 1995.

(23) Zaugg, H. E.; Michaels, R. J. *J. Org. Chem.* **1974**, *39*, 351. Mesiters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1655.

(24) Ebner, J.; Reily, D. In *Active Oxygen in Chemistry*; Foote, C. S., Silverstone-Valentine, J., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: Glasgow, 1995. Oxidations of this type are conveniently carried out as described in: Wheeler, T. N.; Craig, T. A.; Morland, R. B.; Ray, J. A. *Synthesis* **1987**, 883.

(25) Friedman, L. *Org. Synth.* **1963**, *43*, 80.

(26) Caruso, A. J.; Lee, J. L. manuscript in preparation.

(27) *T*<sub>g</sub>'s for the corresponding polyesters based on ethylene glycol and dimethyl terephthalate (PET) and ethylene glycol and dimethyl naphthalene-2,6-dioate (PEN) are 81 and 125 °C, respectively. Yoon, K. H.; Lee, S. C.; Park, O. O. *Polymer J.* **1994**, *26*, 816.

intermediates to the product xanthenes. Bisphenol A (**1**) (50.00 g, 0.219 mol), *m*-cresol (1.0 L, 9.56 mol), and methanesulfonic acid (19.00 g, 0.198 mol) were charged to a 2 L flask equipped with a reflux condenser, nitrogen inlet, and magnetic stir bar. The flask was then heated to 130–150 °C for 24 h. After cooling, the reaction vessel was fitted with a distillation head and most of the *m*-cresol and liberated phenol were distilled away at ~1 Torr. A 95% yield of phenol was obtained in the distillate as judged by quantitative GC using biphenyl as an internal standard. The residue was dissolved in toluene (500 mL), washed with 5% NaOH, and water, dried over MgSO<sub>4</sub>, concentrated under reduced pressure, and distilled through a Vigreux column at 1 Torr to give a fraction boiling at 160–178 °C as a 10:1 mixture of tetramethylxanthene **2** and trimethylxanthene **25** (41.35 g, 91% purity, 0.158 mol, 72% yield) as a waxy white solid. Recrystallization from MeOH afforded an analytical sample of **2**: mp 59–60 °C (lit.<sup>1b</sup> mp 61–62 °C); <sup>1</sup>H-NMR 7.27 (d, *J* = 8 Hz, 2H), 6.86 (br m, 4H), 2.32 (s, 6H), 1.56 (s, 6H); <sup>13</sup>C-NMR 21.0, 32.7, 33.4, 116.7, 123.8, 123.9, 126.0, 127.1, 150.2 ppm; IR 3035, 2969, 2920, 1634, 1615, 1590, 1566, 1498, 1411, 1306, 1264, 1170, 878, 812 cm<sup>-1</sup>; HRMS calcd for C<sub>17</sub>H<sub>18</sub>O 238.1358, found 238.1359. Xanthene **2** was further characterized by its conversion to diester **6** (see below).

**Xanthene 2 and Phenol from Post-Consumer Polycarbonate.** Flakes of post-consumer, crushed polycarbonate milk jug (100 mg, ~0.39 equiv of BPA), *m*-cresol (2.0 mL, 19.1 mmol), and methanesulfonic acid (22 mg, 0.23 mmol) afforded after 20.5 h at 150 °C phenol (72 mg, 0.77 mmol, 98%) and tetramethylxanthene **2** (83.9 mg, 0.35 mmol, 90%).

**Xanthene 2 and Phenol from BPA Tar.** A mixture of BPA tar (10.46 g) consisting of (wt %) 30% BPA **1**, 40% *o*,*p*-BPA; 10% chroman **11**, and a suite of other phenol–acetone condensation products<sup>13</sup> (20%); *m*-cresol (150 mL, 1.435 mol); and methanesulfonic acid (1.482 g, 15.4 mmol) gave after 4.5 h at 150–155 °C and distillation recovered *m*-cresol containing phenol (7.40 g, 78.72 mmol). On the basis of a molar ratio of residual phenol- and acetone-derived components of from 1.5–2.0 in the BPA tar we estimate the yield of phenol to be 86–92%. The pot residue gave upon workup a 41:8:1(HPLC) mixture (9.30 g) of tetramethylxanthene **2**, trimethylxanthene **25**, and the parent 9,9-dimethylxanthene. A portion of this material was vacuum distilled to give a fraction boiling at 160–190 °C (1 Torr) as a 6.8:1 mixture of xanthenes **2** and **25** (7.435 g). A portion of this material (5.00 g, 18.44 mmol of **2**) was converted via catalytic oxidation (see general method below) to 9,9-dimethylxanthene-3,6-dicarboxylic acid (3.574 g, 11.99 mmol, 65%) as a highly insoluble white powder: mp > 326 °C; <sup>1</sup>H-NMR(DMSO-*d*<sub>6</sub>) 13.03 (br s, 2H), 7.68 (s, 4H), 7.56 (s, 2H), 1.61 (s 6H) ppm; <sup>13</sup>C-NMR 166.6, 149.3, 134.2, 130.6, 127.3, 124.4, 116.8, 34.4, 31.9 ppm; IR 2969, 2677, 2568, 1689, 1419, 1300 cm<sup>-1</sup>; HRMS calcd for C<sub>17</sub>H<sub>14</sub>O<sub>5</sub> 298.0840, found 298.0841.

**Xanthene 2 and Phenol from Chroman 11.** Chroman **11** (100.0 mg, 0.373 mmol), *m*-cresol (2.0 mL, 19.1 mmol), and methanesulfonic acid (19 mg, 0.20 mmol) gave after 39 h at 150 °C phenol (38.5 mg, 0.41 mmol, 55%) and 3,6,9,9-tetramethylxanthene **2** (34.2 mg, 0.14 mmol, 19%).

**Preparation of Spiroketal 24.** A three-neck, 2.0 L flask equipped as in the general example above was charged with bisphenol A (**1**) (105.30 g, 0.461 mol), *m*-cresol (1020.68 g, 9.438 mol) and tetradecane (61.32 g, 0.309 mol, GC ISTD). The mixture was warmed to 100 °C, and methanesulfonic acid (1.53 g, 0.016 mol) was added. The mixture was then heated at 150 °C for 10 h. At this point, gas chromatography of the reaction mixture revealed a 3.4:1 mixture of tetramethylxanthene **2** and spiroketal **24**. Excess *m*-cresol was distilled off at 1 Torr. The pot residue was dissolved in toluene, washed with 10% NaOH solution, water, and brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure to give the crude product as a dark brown oil (76.43 g). A portion of this material (3.10 g) was subjected to column chromatography on silica gel (152 g) in hexane–toluene (6:1) to give spiroketal **24** (502 mg, 1.49 mmol, 24% contained yield). Recrystallization (MeOH) gave an analytical sample: mp 125–131 °C (lit.<sup>1b</sup> mp 125.5–127.5 °C; 132–133 °C, dimorphic solid); <sup>1</sup>H-NMR 7.20 (d, *J* = 8 Hz, 2H),

6.76 (d, d, *J* = 2, 8 Hz; 2H), 6.50 (br d, *J* ≈ 2 Hz, 2H), 1.98 (s, 6H), 2.08 (d, *J* = 14 Hz, 2H), 1.95 (d, *J* = 14 Hz, 2H), 1.60 (s, 12H) ppm; <sup>13</sup>C-NMR 150.2, 136.8, 128.4, 126.1, 122.4, 118.0, 97.7, 46.7, 32.5, 32.3, 30.5, 20.9 ppm; IR 2968, 2936, 1625, 1581, 1512, 1144, 1030, 889, 812 cm<sup>-1</sup>; HRMS calcd for C<sub>23</sub>H<sub>28</sub>O<sub>2</sub> 336.2089, found 336.2084.

**Xanthene 2 from Spiroketal 24.** Spiroketal **24** (54 mg, purity = 97%, 0.155 mmol) was heated at 145–150 °C for 22 h with a stock solution of *m*-cresol containing methanesulfonic acid (MSA) (2.0 mL, [MSA] = 19 mg/mL). After cooling, the reaction mixture was assayed quantitatively by GC for tetramethylxanthene **2** (101.5 mg, 0.43 mmol, 92%).

**Conversion of Chroman 23 to Tetramethylxanthene 2.** Chroman **23**<sup>15</sup> (100 mg, 0.34 mmol), *m*-cresol (2.0 mL), methanesulfonic acid (23.9 mg, 0.25 mmol), and tetradecane (100.7 mg) were heated at 150 °C for 21.5 h, at which time quantitative gas chromatography indicated complete conversion to **2** (151.7 mg, 0.64 mmol, 94%).

**2,7,9,9-Tetramethylxanthene (3).** BPA (103.10 g, 0.452 mol), methanesulfonic acid (20.28 g, 0.21 mol), and *p*-cresol (2.0 L) afforded after workup crude xanthene **3** (147.7 g) as a dark oily solid. Vacuum distillation (~1 Torr) gave a fraction boiling at 138–140 °C shown by GCMS to be a 10:1 mixture (15.37 g) of xanthene **3** (13.99 g, 58.8 mmol, 13%) and 2,9,9-trimethylxanthene. Recrystallization (MeOH) afforded an analytical sample: mp 95–96 °C; <sup>1</sup>H-NMR 7.16 (br d, *J* ≈ 2 Hz, 2H), 6.95 (d, d, *J* = 2, 8 Hz, 2H), 6.90 (d, *J* = 8 Hz, 2H), 2.30 (s, 6H), 1.59 (s, 6H) ppm; <sup>13</sup>C-NMR 21.1, 32.6, 34.0, 116.2, 126.6, 128.1, 129.8, 132.1, 148.5 ppm; IR 2972, 2926, 1488, 1297, 1258, 816 cm<sup>-1</sup>; HRMS calcd for C<sub>17</sub>H<sub>18</sub>O 238.1358, found 238.1364. This material was further characterized by its conversion to diester **7**.

**Tetramethylxanthene 3 from Acetone and *p*-Cresol.** Acetone (397 mg, 6.84 mmol), *p*-cresol (10.34 g, 95.6 mmol), and MSA (122 mg, 1.27 mmol) were heated at 135 °C for 90 h. The reaction mixture was diluted with toluene (50 mL), washed with 10% NaOH solution (3 × 100 mL) and water, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure to afford crude xanthene **3** (1.122 g) as a dark oil that crystallized upon exposure to a trace of crystalline **3**. Recrystallization (MeOH) gave pure **3** (583 mg, 2.45 mmol, 36%), mp 95–96 °C.

**2,6,9,9-Tetramethylxanthene (4) (as a Mixture with Xanthenes 2 and 3).** Bisphenol A (27.36 g, 0.12 mol), *m*-cresol (150 mL, 1.43 mol), *p*-cresol (150 mL, 1.43 mol), and methanesulfonic acid (2.96 g, 30.9 mmol) gave an oily melange of tetramethylxanthenes **2**, **3**, and **4** (21.89 g). A portion of this material (19.89 g) was distilled (~1 Torr) to give a fraction boiling at 160–175 °C, which was shown by GCMS to consist of a 1.9:1:4.8 mixture of xanthenes **2**, **3**, and **4** (17.742 g, 75.4 mmol, 62%), respectively, containing 3,9,9-trimethylxanthene (**25**) and 2,9,9-trimethylxanthene as the principal impurities. The identity of xanthene **4** in this mixture was confirmed by its conversion to pure diester **8** (see below).

**2,3,6,7,9,9-Hexamethylxanthene (5).** BPA (100.0 mg, 0.439 mmol), 3,4-dimethylphenol (2.000 g, 16.39 mmol), and MSA (20 mg, 0.21 mmol) were heated at 100 °C for 40 h. The product mixture was diluted with toluene, washed with 10% NaOH and water, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure to give **5**<sup>2</sup> (67.3 mg, 0.25 mmol, 57%) as a brown solid: <sup>1</sup>H-NMR 7.12 (s, 2H), 6.81 (s, 2H), 2.23 (s, 6H), 2.22 (s, 6H), 1.59 (s, 6H) ppm.

**Hexamethylxanthene 5 from Acetone.** A mixture of 3,4-dimethylphenol (1.50 kg, 12.2 mol), acetone (47.30 g, 0.815 mol), and methanesulfonic acid (9.45 g, 98.3 mmol) was heated at 100–120 °C for 120 h and then at 150 °C for 7 h. Removal of excess 3,4-dimethylphenol by distillation (~1 Torr) and workup gave a dark waxy solid that was placed on a fritted funnel and washed with MeOH to afford a 4.8:1 mixture (100.99 g) of hexamethylxanthene **5**<sup>2</sup> and 4,4,4',4',6,7,6',7'-octamethylspirobichroman (**34**).<sup>16</sup> This product mixture was used to prepare tetraester **9** (see below). The mixture (10.00 g) was slurried in boiling methanol (300 mL) and filtered on a fritted funnel. The filtrate was set aside and afforded grayish crystals (5.02 g) of a 7:1 mixture of hexamethylxanthene **5** and **34**. The methanol-insoluble solid was

again slurried in boiling MeOH, filtered, and air dried to give pure **34** (330 mg, 0.91 mmol) as a snow white solid: mp 197–199 °C (lit.<sup>16</sup> mp 199–200 °C); <sup>1</sup>H-NMR 7.04 (s, 2H), 6.48 (s, 2H), 2.18 (s, 6H), 2.09 (s, 6H), 2.05 (d, *J* = 13.8 Hz, 2H), 1.92 (d, *J* = 13.8 Hz, 2H), 1.59 (s, 6H), 1.33 (s, 6H) ppm; HRMS calcd for C<sub>25</sub>H<sub>32</sub>O<sub>2</sub> 364.2402, found 364.2428.

**General Procedure for Oxidation and Esterification of Xanthenes 2–5. Dimethyl 9,9-dimethylxanthene-3,6-dicarboxylate (6).** Tetramethylxanthene **2** (11.88 g, 90% purity, 44.9 mmol), Co(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (127 mg, 0.51 mmol), Mn(OAc)<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub> (128 mg, 0.52 mmol), di-*tert*-butyl peroxide (248 mg, 1.70 mmol), 48% HBr (248 mg), and acetic acid (125 mL) were charged to a 500 mL autoclave equipped for stirring and pressurized to 300 psi with oxygen. The stirred mixture was maintained at 130–170 °C for 4 h. The reaction is sufficiently exothermic to generate an internal temperature of 160–170 °C once it initiates at about 130 °C. Additional O<sub>2</sub> was added to maintain an internal pressure of 250–300 psi. After cooling, the vessel was vented and the product collected on a fritted funnel and washed with water to give after air drying 9,9-dimethylxanthene-3,6-dicarboxylic acid (10.456 g, 35.1 mmol, 78%) as a white solid, mp > 326 °C. The diacid (8.870 g, 29.7 mmol), methanol (225 mL), and concentrated H<sub>2</sub>SO<sub>4</sub> (1.5 mL) were heated to reflux for 8 h. The reaction mixture was cooled in an ice bath, and the orange crystalline solid was collected by filtration, washed with water, and air dried to afford ester **6** (8.62 g, 26.4 mmol, 90%). Recrystallization (*i*-PrOH) afforded an analytical sample: mp 154–155 °C; <sup>1</sup>H-NMR 1.65 (s, 6H), 3.93 (s, 6H), 7.47 (d, *J* = 8 Hz, 2H), 7.73 (br s, 2H), 7.75 (d, *J* = 2, 8 Hz, 2H) ppm; <sup>13</sup>C-NMR 31.9, 34.7, 52.2, 117.8, 124.4, 126.2, 129.7, 134.5, 150.1, 166.4 ppm; IR 2975, 2955, 1712, 1105, 1005, 932, 768 cm<sup>-1</sup>; HRMS calcd for C<sub>19</sub>H<sub>20</sub>O<sub>5</sub> 326.1154, found 326.1150. Concentration of the filtrate afforded additional diester **6** (0.47 g) of lower purity (81.2% pure by HPLC).

**Dimethyl 9,9-Dimethylxanthene-2,7-dioate (7).** Tetramethylxanthene **3** (14.36 g, 91.5% purity, 55.2 mmol) gave 9,9-dimethylxanthene-2,7-dicarboxylic acid (15.22 g, 51.0 mmol, 92%) as a white solid that was fully characterized as its dimethyl ester **7**. The diacid (10.00 g, 33.5 mmol) gave diester **7** (5.72 g, 17.5 mmol, 52%) as an off-white crystalline solid: mp 150–151 °C; <sup>1</sup>H-NMR 8.15 (d, *J* = 2 Hz, 2H), 7.91 (d, *J* = 2, 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 3.92 (s, 6H), 1.69 (s, 6H) ppm; <sup>13</sup>C-NMR 32.8, 34.1, 52.1, 116.6, 125.5, 128.7, 129.3, 129.6, 153.2, 166.5 ppm; IR 2978, 1715, 1609, 1578, 1447, 1259, 1130, 1112, 912, 843 cm<sup>-1</sup>; HRMS calcd for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub> 326.1154, found 326.1180. The filtrates afforded additional diester **7** (2.87 g, 8.8 mmol, 26%).

**Dimethyl 9,9-Dimethylxanthene-2,6-dioate (8).** A 1.8:1.0:4.8 mixture of xanthenes **2**, **3**, and **4** of 90% purity (14.50 g, 54.8 mmol) was oxidized to afford a mixture of the corresponding acids, 9,9-dimethylxanthene-3,6-dicarboxylic acid, 9,9-dimethylxanthene-2,7-dicarboxylic acid, and 9,9-dimethylxanthene-2,6-dicarboxylic acid, as a cream-colored solid (12.28 g, 41.2 mmol, 75%) having a mp > 300 °C. A portion of this material (4.137 g, 13.87 mmol) was esterified in MeOH to afford the product diesters (4.05 g) as a 1:4.2:1.2 mixture of dimethyl 9,9-dimethylxanthene-2,7-dicarboxylate (**7**), dimethyl 9,9-dimethylxanthene-2,6-dicarboxylate (**8**), and dimethyl 9,9-dimethylxanthene-3,6-dicarboxylate (**6**) as a cream-colored solid. The crude product was recrystallized twice from methanol to afford pure dimethyl 9,9-dimethylxanthene-2,6-dicarboxylate (**8**) (465 mg, 1.42 mmol, 10%): mp 145–147 °C; <sup>1</sup>H-NMR 8.14 (d, *J* = 2 Hz, 1H), 7.91 (d, *J* = 2, 8.5 Hz, 1H), 7.78 (d, *J* = 1.8, 8.1 Hz, 1H), 7.74 (br d, *J* ≈ 2 Hz, 1H), 7.49

(d, *J* = 8 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H) 1.68 (s, 6H) ppm; IR 2975, 2950, 1730, 1720, 1615, 1605, 1575, 1442, 1435, 1417, 1275, 1208, 1122, 1078, 1000, 940, 922, 892, 829, 763, 728 cm<sup>-1</sup>; UV (MeOH) λ = 245 nm (log ε = 4.35), 272 nm (log ε = 4.26); HRMS calcd for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub> 326.1154, found: 326.1138.

**Tetramethyl 9,9-Dimethylxanthene-2,3,6,7-tetracarboxylate (9).** To a high-pressure bomb equipped for stirring was added Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O (188 g, 630 mmol), water (200 mL), and a 4.8:1 mixture of hexamethylxanthene **5** and **34** (44.80 g total, 34.85 g, 130.8 mmol of **5**). The reactor was sealed and heated to 250 °C under autogenous pressure at ~600 psi for 19 h. Upon cooling, the reaction mixture was filtered to give recovered starting material (23.2 g as a 4.2:1 mixture of xanthene **5** and **34**) and a homogeneous aqueous filtrate that was acidified with 10% HCl to afford pure 9,9-dimethylxanthene-2,3,6,7-tetracarboxylic acid as a cream-colored solid (21.2 g, 54.9 mmol, 42%): <sup>1</sup>H-NMR(DMSO-*d*<sub>6</sub>) 8.20 (s, 2H), 7.64 (s, 2H), 1.68 (s, 6H). Esterification of a portion (15.25 g, 39.5 mmol) of this material afforded tetraester **9** (8.26 g, 18.7 mmol, 47%) as a light green solid: mp (DSC) 152 °C; <sup>1</sup>H-NMR 7.89 (s, 2H), 7.35 (s, 2H), 3.93 (s, 6H), 3.92 (s, 6H), 1.68 (s, 6H) ppm; IR 1719, 1549, 1431, 1398, 1286, 1116, 782 cm<sup>-1</sup>; <sup>13</sup>C-NMR 167.3, 166.7, 151.3, 132.9, 131.4, 128.2, 126.2, 117.0, 52.6, 52.5, 34.2, 32.3 ppm; HRMS calcd for C<sub>23</sub>H<sub>22</sub>O<sub>9</sub> 442.1264, found 442.1268.

**Poly(ethylene 9,9-dimethylxanthene-3,6-dioate) (33).** Diester **6** (2.0002 g, 6.13 mmol), ethylene glycol (571.5 mg, 9.21 mmol), and tetraethyl hexyltitanate (4.9 μL) were charged to a 25 mL two-necked round-bottom flask equipped with a mechanical stirrer, short-path distillation head, receiving flask, and nitrogen inlet. The reaction vessel was purged with nitrogen and then lowered into a salt bath preheated to 180 °C. Methanol began to distill over slowly. After 45 min at 180 °C, the bath temperature was raised to 250–280 °C and held there for 0.5 h. After 45 min, the apparatus was attached to the house vacuum (*P* = 40–100 Torr). The reaction mixture was visibly more viscous as the remaining excess ethylene glycol distilled into the receiver. After 30 min at the slightly reduced pressure (*P* = 40–100 Torr), the apparatus was evacuated (*P* = 1 Torr). The contents of the reaction vessel became very viscous, and after 45 min at 1 Torr as much of the polymer as possible was pulled using a spatula from the hot reaction vessel under a plume of nitrogen. The strands of product removed were immediately immersed in water and subsequently air dried to give polyester **33** (1.48 g, 74% of theory, slightly yellow glass), which gave upon compression at 280 °C on a Carver press a tough, clear film: *T*<sub>g</sub> = 163.7 °C; GPC gave *M*<sub>n</sub> = 77 970; *M*<sub>w</sub> = 241 700. The product was soluble in chloroform: <sup>1</sup>H-NMR 7.76 (d, *J* = 2, 8 Hz, 2H), 7.73 (br s, 2H), 7.45 (d, *J* = 8 Hz, 2H), 4.66 (s, 4H), 1.62 (s, 6H) ppm; <sup>13</sup>C-NMR 32.0, 34.7, 62.9, 117.9, 124.5, 126.3, 129.4, 134.7, 150.1, 165.6 ppm.

**Supporting Information Available:** Copies of <sup>1</sup>H-NMR data for compounds **2**, **3**, **5–9**, **24**, **33**, and **34** and <sup>13</sup>C data for **24** and 9,9-dimethylxanthene-3,6-dicarboxylic acid (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. This material can also be requested directly from the author.

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