Aromatic Polyesters with Large Cross-Planar Substituents

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ABSTRACT: Polyesters were synthesized by the interfacial and solution methods from aliphatic and aromatic diacid chlorides and bisphenols having essentially planar, doubly attached groups on the methylene unit between the phenylene rings. The planar units were 1-indanylidene, 1,1-phthalan, 9-fluorenylidene, 9-(9,10-dihydroanthracenylidene), and 9-anthronylidene. All of the polymers had T_g values and softening temperatures far above those of the corresponding polyesters based on 2,2-bis(4-hydroxyphenyl)propane and many of them softened at higher temperatures than like polymers from phenolphthalein or polyesters with large three-dimensional substituents. These results show that neither the polar character of a lactone substituent nor the bulkiness of a three-dimensional substituent are needed to attain a high softening temperature. The polymers were soluble in many common solvents. The antagonistic solvent effect, reported previously for polyesters from phenolphthalein, was also observed for some members of this new group of polyesters. Fibers from the polyterephthalate of 9,9-bis(4-hydroxyphenylfluorene) exhibited good thermal stability, being undamaged after 100 hr at 300° in air.

Discussion and Results

A great many polyesters have been synthesized from bisphenols having two phenylene rings connected by a carbon atom bearing various substituents, R and R'.



Most commonly R and R' have been hydrogen, alkyl groups, and phenyl groups. The two groups have also been combined to form cyclohexylidene and cyclopentylidene units. Several years ago in this laboratory derivatives of phenolphthalein and similar compounds were investigated as polyester intermediates.^{1,2} In these structures the connecting group between the phenylene rings is an essentially planar, polar unit standing crosswise of the polymer chain. It was found



that these structures imparted marked increases in T_{μ} values and softening temperatures of the polymers and that solubility in low-boiling solvents was greatly enhanced. Whether the rise in thermal transitions was due to the polarity of the groups, their bulk, or steric hindrance was not established. A common fault for utility in fibers was the failure of the compositions to crystallize.

Shortly thereafter Jackson and Caldwell³ published a report on polycarbonates based on bisphenols from norbornanone and more complex three-dimensional connecting units. In this case too, increases in T_g



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(2) P. W. Morgan, J. Polym. Sci., Part A, 2, 437 (1964).

(3) W. J. Jackson and J. R. Caldwell, *Ind. Eng. Chem.*, *Prod. Res. Develop.*, 2, 246 (1963).

and distortion temperature were realized. The change was attributed to the restriction of rotation of the phenylene units by the bulky connecting group.

A type of connecting structure not yet examined was the planar, nonpolar group. Synthesis and use of this type of bisphenol would answer the unsettled question of a polarity effect in the phthaleins and would provide a new group of intermediates whose symmetry could lead to easier crystallization, good hydrolytic stability, and unusual elevation of thermal transitions.

Bulky bisphenol connecting units which were used in this study are shown in Table I.

Since this work was carried out, Korshak and his coworkers and Smirnova and coworkers have explored the preparation and behavior of several polyesters of fluorenebisphenol **5** in great detail.^{4–16} They have also

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TABLE I CONNECTING STRUCTURES USED IN FORMATION OF BISPHENOLS



recently reported on some polyesters from anthrone bisphenol 9.17

Bisphenol Synthesis. The most common bisphenol synthesis is the condensation of a ketone with excess phenol in the presence of an acidic condensing agent. In this work a small amount of an organic thiol was found to be an effective cocatalyst in many cases.^{3, 18} The multiring ketones exhibited widely differing reactivity toward phenol. Fluorenone was surprisingly reactive, giving high yields in a short time by an exothermic reaction. The resulting structure **10** has four phenyl rings attached to one carbon atom and yet is highly stable thermally and chemically.



Whenever the direct dehydration reaction between the ketone and phenol did not proceed readily, the alternate condensation of a dichloride and phenol under anhydrous conditions was often successful. The dichlorides were prepared readily from the ketone and thionyl chloride or other known routes.

Polymer Synthesis. Interfacial polycondensation was used in nearly all preparations. A major difficulty with the use of bisphenols bearing large substituents is

the low solubility of the phenoxide in water. The addition of the accelerator, tetraethylammonium chloride, to the alkaline solution often caused additional precipitation. A solution to the problem in many instances was to add a 100% excess of sodium hydroxide in which the phenol was soluble and was not precipitated by accelerator. Dihydroxytetraphenylmethane did not respond to this treatment and was used as a solid dispersion. Low molecular weight polymers resulted.

The importance of completely dissolving the bisphenol is shown by comparing two preparations of polymer from fluorenebisphenol and 5-chloroisophthaloyl chloride. When equivalent alkali was used and the bisphenol dispersed but did not dissolve, the inherent viscosity (see fcotnote *a*, Table II) of the polymer was 0.46; when a 100% excess of alkali was used, the viscosity was 0.93.

Because excess alkali causes increased hydrolysis of the diacid chloride, polyesters from aliphatic diacid chlorides were obtained in higher molecular weights, and sometimes greater yields, by adding an excess of diacid chloride in small increments after the initial polymerization was complete. Additional alkali was added if the system became neutral or acidic. For example, fluorenebisphenol was dissolved with 100% excess NaOH and was allowed to react with adipyl chloride equivalent to bisphenol. The η_{inh} was 0.14 (97%); when excess acid chloride was also used, the η_{inh} was 0.97 (98%).

A simple alternative to the interfacial procedure is a low-temperature solution method with a tertiary amine acid-acceptor.^{1,2} Keys to success are the use of pure, inert solvents for the intermediates and polymer, cooling, and gradual addition of the acid chloride solution. The method is applicable to use with aliphatic diacid chlorides (see Experimental Section) although the shorter chain intermediates are more difficult to employ. The solution method was of value when the bisphenols did not readily dissolve in aqueous alkali, as with 4,4'dihydroxytetraphenylmethane, discussed above. In this case alcohol-free chloroform, a polymer solvent, was used.

Solubility of Polymers. The majority of the polymers with cross-planar substituents, described in Tables II and III, were soluble in such solvents as *m*-cresol, *sym*-tetrachloroethanephenol, chloroform, 1,2-dichloroethane, tetrahydrofuran and pyridine. The ease and range of solubility was not as great as for polyesters of phenolphthalein.²

Chlorobromomethane and 1-chloro-2-bromoethane were found to be better solvents than the related dichloro compounds. For spinning and film casting they possess the advantage of increased boiling temperature.

The antagonistic solvent effect observed for phenolphthalein polyesters^{1,2} was found for several of the present polyesters, including both those with hydrocarbon substituents and those with ether and carbonyl groups in the bisphenol substituent. The nature of this effect is that two solvents for a polymer, one of which is a hydrogen donor and the other a hydrogen acceptor, exhibit much lowered solvent power in combination than separately. The appearance of this

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⁽¹⁸⁾ R. P. Perkins and F. Bryner, U.S. Patent 2,359,242 (Sept 26, 1944); German Patent 905,977 (March 8, 1954).

R in bisphenol	Acid chloride	Yield, %	$\eta_{ ext{inh}}{}^a$	Softening temp, °C ^b	DTA endotherms,° °C
Isopropylidene	Phosgene		2.4	220-230	
	Sebacyl		0.56	< 50	
	Isophthaloyl		1.86	280	140
	Terephthaloyl		1.59	350	238, 343
Cyclohexylidene	Phosgene		0.4	250-260	
	Sebacyl	89	0.73	160	
	Terephthaloyl	89	0.51	380	275
Ethylphenylmethylene	Phosgene	81	0.24	180	147
	Sebacyl	95	0.53	Ca. 100	88
	Terephthaloyl	98	0.56	310	243
1,1-Phthalide	Phosgene		0.86	360 dec	
	Sebacyl		0.60	190	
	Terephthaloyl		1.12(1.44)	>400	263, 356
2-Norbornylidene	Phosgene		>1.2		224 ^{<i>d</i>}
Diphenylmethylene	Phosgene	91	0.56	240	220
	Sebacyl	94	0.35	120	
	Terephthaloyl	89	0.40 (0.60)	>400	210, 280
1-Indanylidene	Phosgene	100	1.64	295	219
	Sebacyl		0.57	160	
	Terephthaloyl	88	0.46	>360	312
Phthalan	Sebacyl	93	0.66	210	
	Terephthaloyl	95	1.38	360	312
9-Fluorenylidene	Phosgene	9 6	0.85*	~390	355
	Dimethylmalonyl	84	0.12	218	
	Succinyl	97	1.04	350	234
	Glutaryl	92	0.89	264	207
	Adipyl	98	0.97	218	166
	Suberyl	92	0.54	190	158
	Azelayl	98	0.59	181	150
	Sebacyl	100	0.60 (0.73)	175	151
	Undecandioyl	88	0.41	158	136
	Dodecandioyl	94	0.78	180	117
	Isophthaloyl	100	0.77	>360	
	5-Chloroiso- phthaloyl	92	0.93	355	
	5- <i>t</i> -Butyliso-	95	0.49	350	
	phthaloyl	0.2	1 40	. 100	29.5
		93	1.40	>400	203
	terephthaloyl	91	1.34	> 300	
	Terephthaloyl- sebacyl (60–40)	91	0.74	350	
-Xanthenylidene	Sebacyl	96	0.59	186	
	Terephthaloyl	9 0		>360	252
9-Anthronylidene	Phosgene	83	0.31	263	
	Succinyl	87	0.60	252	
	Adipyl	94	0.64	242	
	Sebacyl	98	1.12	232	
	Dodecandioyl	100	1.42	200	400
	l erephthaloyl Isophthaloyl	92 95	0.88 (0.99) 1.99	375	400
-Dihydroanthraceny-	Sehacyl	100	1.03	192	134. 197
	Scoacyr	100	1.05	> 100	247
lidene	Terephthaloyl	97	0.93	>400	342
lidene	Terephthaloyl	97	0.93	>400	542

TABLE	11
PREPARATION OF	POLYESTERS

		TABLE II (Contin	uea)		
R in bisphenol	Acid chloride	Yield, %	$\eta_{ ext{inh}}{}^a$	Softening temp, $^{\circ}C^{b}$	DTA endotherms,° °C
Spiro[fluorene-9,9'-	Phosgene	85		>400	295
xanthene]	Sebacyl	97	0.62	205	
	Terephthaloyl	98	0.89°	>400	29 0

^a η_{inh} , the inherent viscosity, is $[\ln \eta_{rel}]/c$ at 30° where c is the polymer concentration of 0.5 g/100 ml. Except as noted, the solvent was *sym*-tetrachloroethane-phenol (40-60 by weight); values in parentheses are for polymerization by low-temperature solution method. ^b Determined on a gradient hot bar using powdered, dry polymer and light, sliding pressure. See ref 1, p 471. ^c Heating rate 10°/min under N₂. Readings taken at endotherm maximum rather than initiation point. ^d T_g from Jackson and Caldwell.³ ^e Determined in pyridine. ^f Determined in *m*-cresol.

TABLE III

A. Alternating Copolycarbonates^a

R in bisphenol	Bischloroformate	$\eta_{ ext{inh}}$	Softening temp, °C
9-Fluorenylidene	Hydroquinone	0.93	296
	2,2-Bis(4-hydroxyphenyl)propane		350
	2,2-Bis(4-hydroxy-3,5-dichlorophenyl)propane	0.49	290
	2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane	0.21	280
	2,2-Bis(4-hydroxyphenyl)hexafluoropropane	0.30	264

D. Kandom copolycal bollate	В.	Random	copolycarbonate
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First bisphenol	Second bisphenol	Mole ratio	$\eta_{ ext{inh}}$	Softening temp, °C
9-Fluorenylidene	2,2-Bis(4-hydroxyphenyl)propane	80-20	0.56	278
		50-50	0.3	228
	2,2-Bis(4-hydroxy-3,5-dichlorophenyl)propane	80-20	0.62	275
		50-50	0.15	254
	Bis(4-hydroxyphenyl) ketone	80-20	0.50	268
9-Anthronylidene	Bis(4-hydroxyphenyl) ether	8020	0.24	240
9-Fluorenylidene	9-Anthronylidene	70-30	0.48	268
		60-40	0.38	299
		20-80	0.28	245

^{*a*} See footnotes a and b of Table II.

phenomenon seems to be dependent on having a polymer which had borderline solubility in the individual test solvents.

One sample of the terephthalate of 9,9-bis(4-hydroxyphenyl)xanthene 11 was found to be insoluble in all solvents tried. The polymer probably was cross-linked as a result of opening the ether link by a number of different alkaline and acid treatments of the bisphenol in attempts to force it into solution.



A similar difficulty was encountered with polymers derived from 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] 12. The use of crude bisphenol or forcing the polymerization with excess alkali yielded partially insoluble polymers.



Polyesters prepared from 9,9-bis(4-hydroxyphenyl)-10-hydroxy-9,10-dihydroanthracene **8** were soluble in fewer solvents than usual but were soluble in m-cresol and tetrachloroethane-phenol mixtures.

Thermal Transitions and Melting of Polymers. All of the polyesters bearing large planar substituents described in this work softened at much higher temperatures than the corresponding esters from 2,2-bis(4hydroxyphenyl)propane. Many of them softened at higher temperatures than the phthalide structures. Figure 1 illustrates the effect with three series of esters from aliphatic diacids. The effect is further shown by the listing of softening temperatures and DTA endotherms in Tables II and IV.

The results show that large substituents of a planar type will produce increases in softening points of the

Bisphenol							
central group	DTA endotherms, °C	Major weight loss range, °C	400°		ht loss at 600°	650°	
CH CCH,	238, 343	370-665	1	43	79	97	
$\not \sim$	275, 391, 416	245-652	15.5	43	79	99	
CC ^T H ²	243	395-645	1	32	51	55	
$\overline{\mathbb{Q}}$	312	420660	2.5	14	56	59	
	312, 355	350-640	3	40	51	53	
	263, 356	317-630	2	24	50	52	

 TABLE IV

 THERMAL PROPERTIES OF POLYTEREPHTHALATES

polymers and that these substituents do not need to be bulky in a three-dimensional sense or polar in character. The results, however, also show that polarity is a factor in addition to the size of substituent, for, when similar structures are compared, those bearing carbonyl, ester, or amide groups have the higher softening points. For example, the polycarbonates bearing 1,1-indanylidene **13**, phthalide **15**, and phthalimidine **16** units soften in increasing order, 295° , 360° , $>400^{\circ}$.²



A comparison of the initial softening temperatures of the sebacates based on xanthenylidene (ether bridge,



Figure 1. Variation in polymer-softening temperature with chain length of the aliphatic diacid segment of polyesters from 9,9-bis(4-hydroxyphenyl)fluorene (\Box), phenolphthalein (O), and 2,2-bis(4-hydroxyphenyl)propane (∇).

7), dihydroanthracenylidene (methylene bridge, 6) and anthronylidene (carbonyl bridge, 9) shows little difference between the ether and hydrocarbon structures and an appreciably higher softening temperature for the ketone. The data on phthalan 14 and indan 13 structures are considered inconclusive.

Polymers bearing substituents such as represented by structures 13-16 and ethylphenylmethylene must have an atactic form resulting from the random nature of the polycondensation. This must be considered as a factor in comparisons made with polymers having symmetrically placed substituents. Furthermore, the subjective nature of the softening test, the variation in softening behavior of different compositions and the marked effect of polymer molecular weight on both softening test and DTA results make detailed comparisons of small differences inappropriate. DTA endotherms have purposely not been designated as glass transition temperatures, although they may be that in the lower temperature ranges; for example, the series of values for aliphatic polyesters of fluorenebisphenol in Table II.

Some other specific points of interest are the higher melting range of the indanylidene esters compared to the esters with the related noncyclic methylene unit, ethylphenylmethylene. Comparison of the pairs of polyesters bearing the symmetrical fluorenylidene and diphenylmethylene units shows a similar difference. For some pairs the comparison is clouded by polymer viscosity differences. The sebacate of 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] softened at 205°, whereas the related fluorenylidene analog softened at 175°. Reduction of the mobility of the *p*-phenylene groups in the chain by the constraining ether bond in the spiro structure has affected both the softening temperature and the thermal decomposition of the polyesters (see next section). The terephthalate and isophthalate of this spirobisphenol have been reported. 19

Short-Term Thermal Stability. Thermal gravimetric

(19) V. A. Pankratov, V. V. Korshak, and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1256 (1965).

TABLE V	
THERMAL PROPERTIES OF POLYTEREPHTHALATES	

Bisphenol central group	DTA endotherms, °C	Major weight loss range, °C	 400°	——% weigh 500°	nt loss at— 600°	6 5 0°	
Diphenylmethylene	210, 280	460–600	0	5	47	50	
Fluorenylidene	285	460-640	0	5	37	41	
Xanthenylidene	252	400-650	0.7	5	42	47	
Dihydroanthracenylidene	342	400-560	2	33	48	52	
Anthronylidene	400	400-580	2	2	40	43	
Spiro[fluorenexanthene]		480-700	1	2	20	27	

analyses were carried out primarily with the terephthalates (Tables IV and V and Figure 2). The retention in weight, up to 500° in nitrogen, was greater for most of the polyesters with large, planar hydrocarbon substituents than for those which contained oxygen as carbonyl or ether units in the substituent. Exceptions to this were the xanthenylidene unit which provided good weight retention and the dihydroanthracenylidene polymer which was very poor (Table V). Isopropylidene, cyclohexylidene and ethylphenylmethylene links gave relatively poor stability. On the other hand, diphenylmethylene performed as well as fluorenylidene up to 500° and slightly poorer at higher temperature.

The outstanding performer for weight retention was the polyterephthalate of 3,6-dihydroxyspiro[fluorene-9,9'-xanthene] with only a 27% weight loss at 650° (Table V and Figure 2). All of the samples showed nearly complete weight loss at 600° in air.

Thermogravimetric tests, of course, are only indicators of volatility and tell little or nothing by themselves about melting or retention of useful strength or form at high temperatures.

Preparation of Films. Bright, transparent, flexible films were readily dry cast from most of the polymers with inherent viscosities of about 0.5 or above. Toughness was increased by going to the higher molecular weights, but there was no evidence that films from this class of polymers possessed different film-forming character than polymers with smaller substituents. Films were melt-pressed from the polyesters of fluorenebisphenol and 10-, 11-, and 12-carbon aliphatic acids. Pressing temperatures were from 160 to 180°, which corresponds to the measured softening temperatures.

The densities of clear, solvent-free films, cast from tetrahydrofuran, were determined in a carbon tetrachloride-heptane density-gradient tube at 25° . Typical values for polyterephthalates were phenolphthalein, 1.322; 9,9-bis(4-hydroxyphenyl)fluorene, 1.376; 9,9-bis(4-hydroxyphenyl)anthrone, 1.267. The polyterephthalate of 2,2-bis(4-hydroxyphenyl)propane has a density of 1.24 and the polycarbonate is reported to have a density of 1.20. If preferential absorption of carbon tetrachloride during the density measurements is absent, then a possible reduction of polymer density by the bulky substituents has not occurred.

A 20% solution (by weight) of the polyterephthalate of 9,9-bis(hydroxyphenyl)anthrone in chloroform was cast into a 1-mil film on a glass plate. After air drying and then drying at 80° under vacuum for 24 hr, the film was cut into 1/8-in. strips. Strips were drawn about 100% over a hot plate at 310°. The drawn film strips had low crystallinity as shown by X-ray



Figure 2. Thermogravimetric analysis of polyterephthalates of bisphenols: (A) 3,6-dihydroxy[fluorene-9,9'-xanthene], (B) 9,9-bis(4-hydroxyphenyl)fluorene, (C) 9,9-bis(4-hydroxyphenyl)anthrone, (D) 1,1-bis(4-hydroxyphenyl)diphenylmethane, and (E) 9,9-bis(4-hydroxyphenyl)fluorene. E was conducted in air and the others in nitrogen at a heating rate of $20^{\circ}/min$.

diffraction. A drawn film, held taut in boiling acetone for 8 hr, became cloudy but did not increase in crystallinity.

Preparation of Fibers from Poly(fluorenylidenediphenylene terephthalate) (DPF-T). Fibers were easily dry-spun from a 15% solution of DPF-T (η_{inh} 0.72) in chlorobromoethane. The fiber cross-section had a long dogbone shape. The as-spun fiber had tenacity/ elongation/initial modulus/denier (T/E/M_i/Den.) values of 0.82 g/denier, 14%, 22 g/denier, and 11.4 denier/ filament. Shrinkage in boiling water was 0.13%. The tensile properties are roughly comparable to those of cellulose acetate fibers.

A second spin was made with polymer, having an inherent viscosity of 0.81, dissolved in 1,2-dichloroethane-trifluoroacetic acid (90/10) at 18% solids. The as-spun fiber had $T/E/M_i/Den$. values of 0.79/ 7.6/25/9.7. After drawing 240% at 340° over a 3-in. plate, the $T/E/M_i/Den$. values were 1.78/29/30/ 2.65. The drawn fibers were unoriented and showed only trace crystallinity by X-ray.

Heat-Setting and Thermal Tests on DPF-T Fibers. DPF-T fibers as-spun did not shrink on the hot bar at 365° nor change noticeably for a short time in an oven at 400° in a relaxed condition. This is unusual behavior for a polyester. Physical tests were made on fibers spun from chlorobromoethane as shown below. The undrawn fiber was wound on a small stainless steel bobbin and exposed in a small oven in air (Table VI).

TABLE VI							
DURABILITY	OF	DPF-T	Fiber	AT	300°	IN	Air

Time, days	Tenacity, g/denier	Elongation, %	Initial modulus, g/denier
0	0.82	14	22
3	1.13	11	23
4	1.27	18	22
6	1.15	8	22

The fiber became tan in the first 30 min but remained lustrous and showed no loss in tensile strength after 6 days.

At 400° on a steel bobbin the fiber was colored a pale brown in 20 min but was flexible and strong. At 16 hr, the fiber on the bobbin was decomposed while the fiber lying on glass was crimped. It was flexible but had low tenacity. The onset of decomposition at about 400° was shown also by thermal gravimetric analysis (Figure 2).

Experimental Section

Preparation of Bisphenols. Bis(4-hydroxyphenyl)diphenylmethane. The preparation of this bisphenol from benzophenone was unsuccessful so the method of Gomberg and Jickling²⁰ was used. By this route carbon tetrachloride and benzene were allowed to react with aluminum chloride to form diphenyldichloromethane, which was separated as an orange oil. The oil was combined with two volumes of molten phenol. Hydrogen chloride was evolved spontaneously. After the mixture stood overnight, it was poured into water and the solid was worked up by solution in aqueous alkali and precipitation with acid. Crystallization from acetic acid, including Darco treatment, gave pale yellow needles. The crystals tended to retain acetic acid. Recrystallization from ethanol gave a colorless product melting at 295° dec.

1,1-Bis(4-hydroxyphenyl)indane. 1-Indanone (26.8 g, 0.2 mol), 76 g of phenol (*ca.* 0.8 mol), 1 ml of β -mercaptopropionic acid, and 126 ml of concentrated hydrochloric acid were mixed and heated on a water bath with stirring for 7 hr. The mixture became brownish red as soon as the mercaptan was added and slowly became viscous as the reaction proceeded. After the mixture stood overnight, it was diluted with water. A gum and a yellow solid separated. The solid was recrystallized from ethanol as yellow plates (6 g).

Crystallization from toluene gave long, silky, light yellow needles, which did not melt below 360° and were not soluble in alkali and therefore were not a phenol.

Anal. Calcd for $C_{27}H_{18}$: C, 94.70; H, 5.29. Found: C, 94.11, 94.38, 94.19; H, 5.20, 5.24, 5.20.

Infrared and nmr analysis confirmed the identity of this product as a hydrocarbon trimer from dehydration-cyclization of 1-indanone to truxene (*sym*-tribenzylenebenzene).

The gummy residue was extracted with 20% aqueous sodium hydroxide and the product precipitated with hydrochloric acid. It was recrystallized twice from aqueous acetic acid as a mixture of bright needles and prisms. The yield was 5.0 g (8%), mp 216–217°.

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.41; H, 6.00. Found: C, 83.07, 82.97; H, 6.07, 5.96.

9,9-Bis(4-hydroxyphenyl)fluorene. Fluorenone (36 g, 0.2 mol) was dissolved in 76 g (0.8 mol) of molten phenol. β -Mercaptopropionic acid (1 ml) was added and then dry hydrogen chloride was bubbled in for about 10 min. The

system became very dark but in 2-3 hr it suddenly cleared and was quite viscous. Although this particular preparation was allowed to stand 2 days, the reaction was essentially complete in the first few hours.

The mixture was diluted with water to give a white solid which was collected and washed. The product was further purified by solution in alkali, precipitation with concentrated hydrochloric acid, and washing. Crystallization of the dry material from toluene gave glassy needles and hard kernels. Mechanical separation and further crystallization gave no evidence that there were two products. The total yield was 32.2 g (46%), mp 224° (lit.²¹ mp $223-224^{\circ}$ for product by a different route).

In scale-up preparations (four times that above) the phenol, hydrogen chloride, and cocatalyst were removed by steam distillation. Partially purified bisphenol with lower melting point had some color but would yield high polymers. Minimum heating in a sublimator removed the yellow component, which proved to be strongly bound fluorenone. Yields in some of these preparations were 80–90%.

1,1-Bis(4-hydroxyphenyl)-1-phenylpropane. This bisphenol was prepared in a manner analogous to that used for the fluorene derivative. The excess phenol was steam distilled and the water washed and dried product was recrystallized from toluene and chlorobenzene. The melting point was 180° (lit. ¹⁸ mp 179.7–180.2°, yield 21%).

9,9-Bis(4-hydroxyphenyl)anthrone. Anthraquinone (20.0 g, 0.096 mol), phenol (20.0 g), and stannic chloride (25 g) were placed in a flamed, round-bottomed flask under nitrogen. The mixture was heated at 80° for 18 hr and then diluted with water. The undissolved residue was dissolved in aqueous sodium hydroxide, filtered, and then acidified with concentrated hydrochloric acid. This product was crystallized from ethanol as a slightly colored granular mass: 3.32 g (9%); mp 318–320°. From acetic acid glassy blades were obtained with the same melting point.

Anal. Calcd for $C_{26}H_{18}O_3$: C, 82.52; H, 4.79. Found: C, 82.3; H, 4.8.

This melting point is appreciably above that of several reports in the literature $(305-309^{\circ})$. ²²⁻²⁴

As an alternate and somewhat easier preparation of this bisphenol, 100 g of anthrone in 700 ml of chloroform was cooled in a flask with an ice-water bath and subjected to a slow flow of gaseous chlorine for 30 min. The solvent was evaporated and the product was worked up by crystallization from benzene. The least soluble material was anthraquinone, which was discarded. The desired product, 9,9-dichloroanthrone (40 g, 30%), was obtained as long, yellow needles, mp 132–134°.

The dichloride and 80 g of warm phenol reacted vigorously with evolution of hydrogen chloride to form the anthrone bisphenol in 80% yield. This product was made analytically pure only with considerable difficulty.

9,9-Bis(4-hydroxyphenyl)-10-hydroxy-9,10-dihydroanthracene. 9,9-Bis(4-hydroxyphenyl)-10-anthrone (22.0 g) was placed in a porcelain thimble in a Soxhlet extractor mounted on a 3-l., three-necked flask which in turn was fitted with a stirrer. Anhydrous ether (1120 ml) and 15.17 g of LiAlH₄ were placed in the flask and stirring was begun with gentle heating to reflux on a steam bath. After 20 hr the product in the flask was isolated by destruction of excess LiAlH₄ with water, neutralization with dilute sulfuric

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acid to pH 7, and separation of the ether layer. Recrystallization from 2B ethanol and water yielded 12.4 g (56%) of bisphenol melting at 178–180°.

The infrared spectrum and nmr data were consistent with the conversion of >C==O to >CHOH at the bridge position. *Anal.* Calcd for $C_{28}H_{20}O_3$: C, 82.08; H, 5.30. Found:

C, 81.7; H, 5.60. 9,9-Bis(4-hydroxyphenyl)-9,10-dihydroanthracene. 9,9-Bis(4-hydroxyphenyl)-10-anthrone (16.0 g) was dissolved in 400 ml of *n*-amyl alcohol and heated to reflux with stirring. Sodium metal (20.0 g-atoms) was added in small portions to the stirred, boiling solutions. After addition and solution of the sodium, the solution was cooled, poured into water, and neutralized with glacial acetic acid. The bisphenol was isolated by extraction with methylene chloride and evaporation to dryness. The product was recrystallized from aqueous ethanol and melted at $248-249^{\circ}$; the yield was 45%.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.68; H, 5.53. Found: C, 85.80; H, 5.50.

The structure was confirmed by the lack of carbonyl and aliphatic hydroxyl bands in the infrared spectrum and by the proportion of hydrogen peaks in the nmr spectrum. Figure 3 compares the carbonyl absorption regions for several polyterephthalates and shows the loss of the aromatic ketone absorption peak at 1670 cm⁻¹ in going from the anthrone (C) to the dihydroanthracene structure (D).

9,9-Bis(4-hydroxyphenyl)xanthene. Xanthone (20 g) was refluxed in 100 ml of thionyl chloride for 5 hr and stood 18 hr to convert it to the dichloride.²⁵ The thionyl chloride was removed under vacuum, the product was washed with petroleum ether and again dried under vacuum. The dichloride was then mixed with 42.2 g of phenol and 0.5 ml of β -mercaptopropionic acid. The mixture was heated on a steam bath for 48 hr. Treatment with water yielded a red oil. The oil dissolved in aqueous sodium hydroxide was allowed to stand for 1 week. A white powder slowly precipitated (5.4 g). This result is presumed to have been due to carbonation from the air.

The bisphenol was recrystallized from warm acetic acid by addition of water to slight turbidity: bright plates, mp 241° , yield 14%.

Anal. Calcd for $C_{25}H_{18}O_3$: C, 81.94; H, 4.95. Found: C, 82.06, 81.92; H, 4.86, 4.84.

3,6-Dihydroxyspiro[fluorene-9,9'-xanthene]. Fluorene (100 g) and resorcinol (200 g) were fused together at 180–200° while dry hydrogen chloride was passed through the melt for 5 hr. The reddish brown product was poured out and cooled and then thoroughly washed with water to remove resorcinol. The bisphenol was crystallized twice from benzene in a glassy, granular form and then melted at 262° (lit.²⁶ mp 232°). The yield was 42%.

Anal. Calcd for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43. Found: C, 82.10, 82.07; H, 4.59, 4.51.

1,1-Bis(4-hydroxyphenyl)phthalan. A phthalanbisphenol could presumably be synthesized from phthalide. However, Schultz and Schnekenburger²⁷ had reported the lithium aluminum hydride reduction of phenolphthalein to a phthalan. A sample was prepared by their method which, after crystallization from aqueous acetic acid, melted at $205-206^{\circ}$ (lit.²⁷ mp 204.8°). A mixture melting point with phenolphthalol was *ca*. 175°. The phthalanbisphenol produced only a trace of color in alklaine solution.



Figure 3. Infrared spectra in the carbonyl region of thin films of polyterephthalates: (A) phenolphthalein, (B) 9,9-bis(4-hydroxyphenyl)fluorene, (C) 9,9-bis(4-hydroxyphenyl)-anthrone, (D) 9,9-bis(4-hydroxyphenyl)-9,10-dihydroanthracene.

Polymer Preparation. Polyterephthalate of 9,9-Bis(4hydroxyphenyl)fluorene. The bisphenol (3.50 g, 0.01 mol), 0.8 g of sodium hydroxide, and 1.5 g of tetraethylammonium chloride monohydrate were dispersed in 120 ml of water in a blender. To this mixture was added quickly with vigorous stirring 2.03 g (0.01 mol) of terephthaloyl chloride in 30 ml of 1,2-dichloroethane. Polymer quickly precipitated on the walls of the blender. After 5 min an equal volume of hexane was stirred in and the precipitated polymer was collected, washed, and dried. The yield was 4.44 g (93%) and the inherent viscosity was 1.40 in *sym*-tetrachloroethanephenol (40–60 by weight).

Since alkali equivalent to the bisphenol was not sufficient to dissolve the phenol completely, other conditions were sought to effect complete solution prior to polymerization. A 100% excess of sodium hydroxide used with heating, stirring, and then cooling was found to form a solution with only slight haze in the above aqueous phase. This was used in a number of subsequent polymerizations.

Polycarbonate of 9,9-Bis(4-hydroxyphenyl)fluorene. A polymerization mixture like that in the first part of the preceding preparation, except for acid chloride, was placed in a blender jar. This included the 1,2-dichloroethane (30 ml). While the mixture was stirred, phosgene was bubbled in from a cylinder until the system was slightly acid. Aqueous, 20% sodium hydroxide (1 ml) was added and phosgene was added again. These steps were repeated. The polymer was dissolved in the dichloroethane and separated as a viscous mass. The polymer was separated by adding 150 ml of hexane with vigorous stirring. The coarse, fibrous product was washed thoroughly with water and dried.

The yield was 3.61 g (96%) and $\eta_{\rm inh}$ was 0.85 (pyridine). The polymer did not melt below 360° but colored slightly at this temperature.

Polysebacate of 9,9-Bis(4-hydroxyphenyl)fluorene. 9,9-Bis(4-hydroxyphenyl)fluorene (3.50 g, 0.01 mol) was suspended in 35 ml of distilled 1,2-dichloroethane in a 250-ml erlenmeyer flask having a ground-glass joint and mounted thereon a 60-ml graduated stoppered addition funnel with

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by-pass. A stirring bar magnet was placed in the liquid and 2.80 ml (0.02 mol) of distilled triethylamine was added from a graduated pipet. A clear solution formed. Sebacyl chloride (2.13 ml, 0.01 mol) was dissolved in 15 ml of 1,2dichloroethane in the addition funnel and the assembly was then set in a small ice-water bath on a magnetic stirrer. While the phenol solution was stirred at medium speed, the acid chloride solution was dripped in over a period of about 40 min. The solution became moderately viscous and a precipitate of triethylamine hydrochloride formed. About 5 ml of solvent was used to rinse in residual acid chloride from the funnel. After 1 hr of reaction time the polymer was precipitated by pouring into hexane (250 ml) and was collected, washed, and dried as in preceding preparations.

The yield was 95% and the inherent viscosity was 0.73.

Other solvents, solvent ratios, and tertiary amine acceptors may be used successfully in this process. In some systems all of the bisphenol may not initially dissolve but will do so as the reaction proceeds and high molecular weight is attained.

Polymer Isolation. Polymers, isolated by a simple series of water or aqueous alcohol washes in a blender, followed by vacuum drying at 80° and storage at room temperature, frequently have been found to undergo a slow degradation in molecular weight over a period of several months or more. This degradation can be overcome or minimized in most

cases by more elaborate isolation treatments, such as mild alkaline washes followed by washing to neutrality, dissolution in an organic solvent and reprecipitation, and use of monophenols as polymer end-capping agents.

Softening Temperatures. As indicated in table footnotes, the polymer softening temperatures were measured on dry powdered or granular polymer on a chrome-plated gradient temperature bar by the application of light sliding pressure. For amorphous or slightly crystalline polymers the softening range is very broad yet the initial point which is recorded here is usually readily determined within several degrees. Similar scales of values can be obtained by penetrometer tests on films and mechanically recorded elongations of films or fibers under light load. All of these measurements are very sensitive to polymer molecular weight, i.e., exhibiting higher softening temperature ranges with increased molecular weight. For more exact studies it would be desirable to seek the maximum softening temperature of each composition by preparing samples of varying molecular weight. Molecular weight distribution should be considered as a possible factor as well.

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Polyquinoxalines Containing Flexibilizing Groups in the Chains

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ABSTRACT: Solution condensations of either 3,3',4,4'-tetraaminodiphenyl sulfone or 3,3'4,4'-tetraaminobenzophenone in combination with various bisbenzils or glyoxals lead to high molecular weight polyquinoxalines. The effect of polymer structure on solubility, glass transition, and decomposition temperatures was investigated. Phenylated polyquinoxalines were readily soluble in chlorinated solvents while their structural nonphenylated analogs were insoluble. Polymer decomposition temperatures ranged between 430 and 520° depending upon structure. Polymer films cast from either chloroform or m-cresol solutions exhibited good toughness and flexibility.

he synthesis of polyquinoxalines²⁻¹⁰ and poly- \mathbf{I} phenylquinoxalines¹¹⁻¹⁴ has been reported by

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several investigators. Polyphenylquinoxalines exhibit superior solubility, and thermal and processing characteristics when compared to their nonphenylated analogs.11,14,15 In addition to the beneficial effect derived from phenyl side group substitution, the introduction of the flexibilizing ether groups into the main polymer chain results in polyquinoxalines of improved melt flow characteristics.16 On the other hand, the presence of ether groups results in a substantial lowering of the oxidative-thermal stability in these polymers.¹⁵ In this investigation we examined some of these effects with polymers containing the chain flexibilizing sulfone and carbonyl groups.

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