Design of Photocrosslinkable Polyesters
with Specific Absorptions*

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Synopsis

2,5-Bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (DVCP), when condensed to form polyesters, polysulfonates, polycarbonates, and polyphosphonates, provides photocrosslinkable polymers useful in photoresist and photolithographic applications. With the use of 26 distyryl ketones related to DVCP, a series of polyesters have been prepared which reflect in their photoresponse the structural variations of the monomeric bisphenols. Those prepared from cyclopentanone are more light sensitive than those from acetone, cyclohexanone, etc. Methoxyl groups on the bisphenol enhance sensitivity and solubility and cause a bathochromic shift. Nitro- and ortho-hydroxyl substituents cause desensitization. Halogens on the bisphenol do not significantly change the polymer sensitivity or absorption. The polymers prepared from DVCP-type bisphenols usually show a hypsochromic shift of 30–40 nm from the monomer's absorption maximum. By selecting the proper bisphenol, one can "tailor" the absorption, sensitivity, and solubility of the resulting polyester. Most of the polyesters of this work were prepared from azelaoyl chloride or sebacyl chloride and had up to 50 mole-% of a nonlight-sensitive bisphenol such as tetrachlorobisphenol A present to improve their solubility in dichloroethane.

INTRODUCTION

Condensation polymers prepared from 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (DVCP) or from bis(4-hydroxy-3-methoxybenzylidene)acetone (DVA) are very sensitive to light and have been found useful in photoresist and in photolithographic applications. Polycarbonates prepared by condensing DVCP or DVA with phosgene or with bischloroformates such as 1,3-bischloroformyloxy-2,2-dimethylpropane were reported by Borden and Unruh.[1] These polycarbonates were prepared by an interfacial condensation in water/methylene chloride with NaOH. Other polycarbonates were prepared from 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone (DVCH). A few polyesters and polyphosphonates were also described. Later, Arcesi described the preparation of related DVCP and DVA polysulfonates[2,3] which showed remarkable resistance to strong caustic etching solutions. The related polyphosphonates and other phosphorous-bearing polymers were prepared by Borden[4] and have shown promise as acid resists:

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DVCP
λ_{max} 404 nm (MeOH)
393 nm (TCE)

DVA
λ_{max} 390 nm (MeOH)
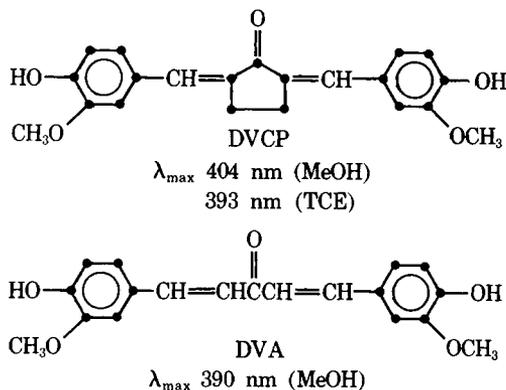
When DVCP or DVA is condensed in solution with diacid chlorides such as sebacyl chloride, high molecular weight polyesters are rapidly formed. If up to 50 mole-% of a solubilizing bisphenol such as tetrachlorobisphenol A is used to replace part of the DVA or DVCP, the resulting polyesters are much more soluble in solvents such as 1,2-dichloroethane (DCE) or 1,1,2-trichloroethane (TCE). The light sensitivity of the polyester is due to the chromophore in the DVCP or DVA. Replacing up to 50% of these monomers does not significantly reduce the photosensitivity of the resulting polyesters. These polyesters are easily prepared by a solution polycondensation process in a mixture of DCE and TCE with triethylamine as the catalyst.[5]

The light sensitivity of the polyester is related to the chromophore present in the monomers, DVA, DVCP, DVCH, etc., which vary in absorption maxima and in relative effectiveness as photocrosslinking agents. In this work, 28 different light-sensitive bisphenols containing either a styryl ketone or bisbenzylidene group as the chromophore have been prepared by condensing aromatic aldehydes with acetone or with cyclic ketones such as cyclopentanone, cyclohexanone, 4-methylcyclohexanone, 4-t-butylcyclohexanone, etc. Of these, 26 monomers were then reacted with various acid chlorides such as azelaoyl chloride, sebacyl chloride, isophthaloyl chloride, etc., to form 100 polyesters. The physical data on the monomers and on 35 selected polymers are presented together with the data on their spectral response. Conclusions are drawn as to the relative effectiveness of the various monomers and to the structural significance of the monomers in forming photocrosslinkable polyesters.

EXPERIMENTAL

The light-sensitive bisphenols were prepared by an acid-catalyzed condensation of the aromatic aldehyde with the ketone. The procedure, described by Samdahl,[6,7] consisted of heating to reflux a mixture of the aldehyde and ketone in absolute ethanol and concentrated hydrochloric acid. If a base-catalyzed Claisen–Schmidt condensation is tried with the hydroxyl-bearing aldehydes, frequently the ketol is isolated. Subsequent treatment with acid will often convert this to the desired α,β-unsaturated ketone or chalcone. Samdahl's method was preferred for the preparation of DVA, but for DVCP and DVCH and the other bisphenols from cyclic ketones, boron trifluoride etherate was used as catalyst. Typical preparations follow.

Preparation of (DVA)

To 4 liters concentrated hydrochloric acid in a 12-liter round-bottomed flask were added 434 g (7 moles) boric acid and 1064 g (7 moles) vanillin. After chilling to 10°C, 560 ml (7.6 moles) acetone was added with stirring. Within 4 min, a heavy, dark precipitate began to form. After standing at 10°C for 5 hr and at 20°C for three days, the mixture was poured into 10 gallons ice water and filtered with suction. After being slurried with three 5-gallon portions of cold water followed by decantation, the product was filtered again on a 29-cm Lapp funnel and washed on the filter with distilled water. After vacuum drying at 70°C for five days, 1126 g (98.5%) of green crystals was isolated. Extraction with ether removed 117 g of material, mp 143°–153°C. Recrystallization of the divanillal acetone from xylene and then from chloroform gave orange needles (664 g), mp 159.5°–160.5°C.

ANAL. Calcd. for $C_{19}H_{18}O_5$: C, 69.9; H, 5.5. Found: C, 69.9; H, 5.5. λ_{max} 390 nm (MeOH).

Infrared absorption at 860, 970, 1000, 1040, 1125, 1130, 1180, 1250, 1275, 1423, 1520, 1580 cm^{-1}; $m/e = 326$, 311 (—CH$_3$), 309 (—OH), 297 (—OCH$_3$), 202, 190, 177, 145, 137, 89, 30. NMR (DMSO) data relative to TMS, δ6.65 ppm aromatic multiplet, 3.40 ppm methoxy methyls, 7.25 and 6.70 olefinic doublet $J_{ab} = 17$ Hz.

Preparation of DVCP

In a 5-liter, three-necked flask equipped with a reflux condenser and a mechanical stirrer, 1218 g (8.0 moles) vanillin and 338 g (4.0 moles) cyclopentanone were mixed with 800 ml absolute ethanol and heated to dissolve the vanillin. Ten milliliters boron trifluoride etherate was added while the solution was hot, causing a deep-green coloration. The reaction mixture was refluxed and stirred for 4 hr after the addition of the catalyst; 1200 ml additional absolute ethanol was added and the reaction mixture was cooled. The product was filtered, washed with three portions of ethanol, and dried at 35°C in the dark. The yield of crude product was 850 g. Two hundred grams of the crystals was dissolved in 4 liters TCE and treated with 5 g Darco activated carbon three times without cooling to separate the product. After the third treatment, the solution was cooled slowly overnight. The crystals were filtered, washed with cold TCE, and recrystallized from 4 liters TCE. The resulting yellow crystals, mp 214.5° to 215.5°C, were filtered and dried in the dark.

ANAL. Calcd. for $C_{21}H_{20}O_5$: C, 71.6; H, 5.7. Found: C, 71.6; H, 6.0. λ_{max} 404 nm (MeOH). 393 nm (TCE).

Infrared absorption peaks at 856, 908, 936, 1000, 1035, 1130, 1175, 1215, 1270, 1450, 1520, 1600, and 1675 cm^{-1}; $m/e = 352$, 351 (–H), 337 (–CH$_3$), 335 (–OH), 321 (–OCH$_3$), 228, 176, 160, 137, 119, 91. NMR (DMSO) data relative to TMS, δ2.52 ppm methylene protons on cyclopentanone ring, 3.35 ppm = methoxy methyls, 6.72 ppm = olefinic protons, singlet, 6.65 ppm = aromatic proton multiplet.

Bisphenols similar to DVA and DVCP often form highly colored addition complexes with the acid used in an acid-catalyzed condensation. The HCl complex of DVA and the BF$_3$ complex of DVCP are both deep green. Recrys-

tallization, as indicated in the preparations above, frees the bisphenol from these complexes.

Both DVA and DVCP and most of the other bisbenzylidene bisphenols of this work are light sensitive, but it is not necessary to prepare them in the dark. However, the polymers derived from these bisphenols should be prepared under gold fluorescent lights and not under white lights.

The following procedure may be used with slight modification to prepare any of the polyesters of this report.

Preparation of Polyester from DVCP, Tetrachlorobisphenol A, and Sebacyl Chloride
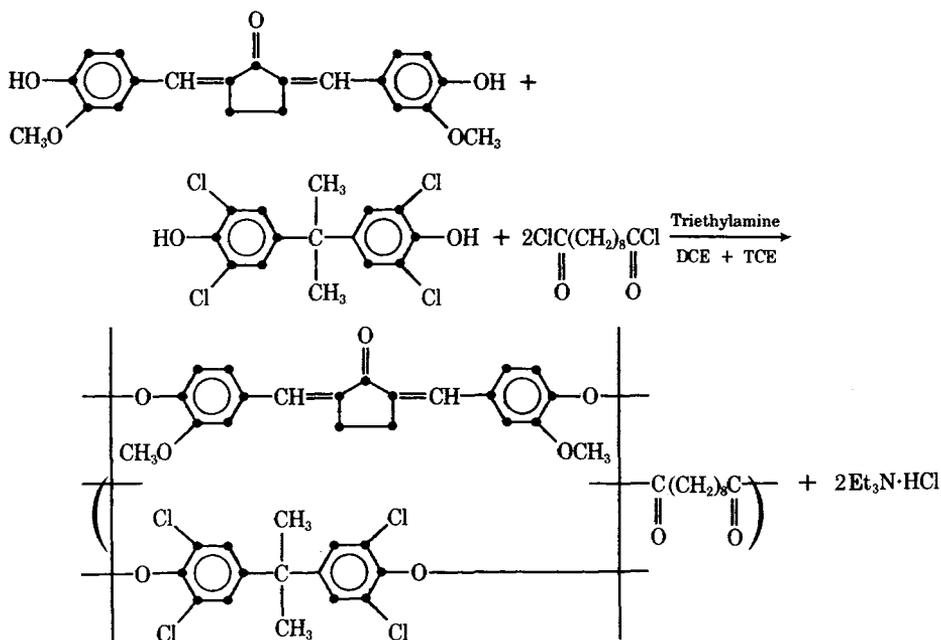
A 500-ml, three-necked flask, fitted with an air-driven paddle stirrer, a reflux condenser, and a dropping funnel, is charged with 150 ml DCE and 25 ml CE (dried over molecular sieves). To this is added a mixture of 10.56 g (0.03 mole) DVCP and 7.32 g (0.02 mole) tetrachlorobisphenol A. While stirring, 12.25 g (0.1125 mole) freshly distilled triethylamine is added which causes the reaction mixture to become bright red with the formation of the DVCP bisphenolate anion. With continued stirring, a solution of 11.95 g (0.05 mole) sebacyl chloride in 10 ml DCE is added dropwise over 3 min, during which time the reaction temperature rises to 61°C. Stirring is continued, and the reaction mixture is heated to reflux (92°C) for 10 min during which time the color changes to yellow and the mixture becomes very viscous. At this time, another 215 ml DCE is added and the mixture is chilled to 5°C. The precipitated amine hydrochloride is filtered off with suction, and the polymer solution is then poured as a fine stream into 4 liters 90% methanol and 10% water with vigorous stirring.

The polyester precipitates as long yellow fibers. These are then decanted and

slurried twice in fresh methanol and in water to remove the last of the salt. After the last filtration, the polyester is air dried at 50°C. Yield 26 g (100%) η_{inh} = 1.09.

ANAL. Calcd for $C_{143}H_{148}Cl_8O_{29}$: C, 65.5; H, 5.9; Cl, 10.8. Found: C, 65.5; H, 5.7; Cl, 10.8. $\overline{M}_n$ = 3272, $\overline{M}_w$ = 125593, λ_{max} = 363 nm (TCE).

Infrared absorption peaks at 610, 725, *808*, 997, *1120*, *1225*, 1414, *1465*, *1503-11*, 1562, 1596, *1610-25*, 1693, *1765*, *2853*, *2930* cm^{-1}. (Italics indicate strong absorption.) NMR (DMSO) relative to TMS, $\delta 2.60$ ppm multiplet for —O—CO—CH$_2$—, 3.08 ppm for methylene protons on cyclopentanone ring, ratio of bisphenol moieties = 59:41 (vs. 60:40 in monomers) in trifluoroacetic acid: $\delta 2.79$ ppm —O—CO—CH$_2$—; 3.23 ppm methylene protons on cyclopentanone, 3.95 ppm = methoxyls on DVCP.

The ultraviolet spectra were run in solution (usually in spectral-grade DCE or in TCE) on a Cary Model 15 spectrophotometer; the infrared spectra were run using a Perkin-Elmer Model 137 sodium chloride infrared spectrophotometer or a Perkin–Elmer Model 467 (high-resolution) grating infrared spectrophotometer. The bisphenols were run as KBr pressings, and the polymers, as films cast on sodium chloride.

Fractional GPC studies were run in a Waters M-200 gel permeation chromatograph using Styragel columns with TCE as the eluant. The weight-average and number-average molecular weights given are in polystyrene equivalent weights. GPC studies of the DVCP polymers invariably show a large oligomeric fraction with a molecular weight of about 1000 which causes the high polydispersity values. In this case, $\overline{M}_w/\overline{M}_n$ = 38.38.

Sensitometry of Polyesters

Evaluation of the photosensitivity of photocrosslinkable polymers was described for poly(vinyl cinnamate) by Minsk and Robertson[8,9] in 1959. Since then, hundreds of new light-sensitive polymers have been disclosed with widely varying absorptions and photosensitivities. Quantitative data must now be obtained by the use of calibrated light sources with emission at wavelengths corresponding to the polymer's principal absorption bands. These data may refer to the amount of crosslinking occurring relative to the amount of incident light, or they may be relative to a change in color, in isomerization, in melting point, or in some other image-forming process.

In this report, these data are not quantified. Each polymer was dissolved (1 g in 50 ml of 1:1 DCE:TCE) and the solutions were filtered. Grained aluminum sheets (5 mils) were cleaned in a vapor degreaser and were then whirl coated with the polymer solutions at 250–500 rpm and the coatings were dried. Exposures were made through a 0.15 density gradient step tablet to a commercial UV source (a Colight "Xposer" with a medium pressure mercury lamp). The light source was not calibrated. The exposure times required to produce a given density of crosslinked polymer were recorded and compared. The exposed coatings were tray developed in mixed solvent (DCE + TCE) and then dyed with the Kodak photo resist black dye, followed by rinsing and drying.

The sensitivity values used in this report (Tables II and III) are strictly qualitative. A value represented by the letter C corresponds to a polymer with

about the same sensitivity as poly(vinyl cinnamate) sensitized with 2-benzoyl-methylen-1-methyl-β-naphthothiazoline. The letters B represent a polymer requiring 10× that exposure; the letters A, 100×; the letters D, 0.5×; and the letters E, 0.1×. Varying the light sources and developing solvents may cause changes in sensitivity values, but the polymers should show the same relative sensitivities. A sensitivity value of 0 indicates that no photocrosslinking was observed at the exposures used.

Wedge spectrograms prepared by the methods of Minsk and Robertson[8,9] indicate the spectral range over which the polymer coating may be effectively insolubilized with a reasonable exposure. Lengthening the exposure often extends this spectral range. Generally, the peak response of the polymer is near its peak absorption. Polymers with absorption peaks in the visible spectrum often show peak response in the UV with a "tail" of insolubilized polymer in the visible spectral region. Effective crosslinking in this visible portion of the spectrum usually requires at least 10× the exposure required for insolubilization in the UV spectrum. Polymers whose peak UV absorption has shifted away from the 313 nm and 366 nm emission lines of mercury sources often show a loss of sensitivity because of lower emission at the other wavelengths by mercury sources.

The polymers of this report show absorption maxima ranging from 326 nm to 378 nm (neglect polymer 23). Under basic conditions, some of the phenolic endgroups are converted to the red phenolate ions with absorptions at 420–480 nm. We have found no evidence of crosslinking by exposures at these wavelengths attributable to the phenolate ions present.

Other Reagents

All the light-sensitive bisphenols of Table I were prepared by the boron trifluoride etherate method described above, except for bisphenols 1–4, which were prepared by Samdahl's method using concentrated hydrochloric acid. In this report, the names of the bisphenols are given in Table I together with the abbreviated names. The abbreviations, such as DVA, DVCP, etc. from Table I are used in the report for simplicity.

The nonlight-sensitive bisphenols used included bisphenol A, mp 157°C (Eastman Organic Chemicals); tetrachlorobisphenol A, mp 132°–4°C (Dover Chemical Co.); tetrabromobisphenol A, mp 182°–4°C (Dow Chemical Co.).

The acid chlorides used included azelaoyl chloride, bp 147°–8°C/8 mm; sebacyl chloride, bp 181°–4°C/16 mm; isophthaloyl chloride, mp 44°–6°C; and terephthaloyl chloride, mp 82°–4°C, all obtained from Eastman Organic Chemicals.

DCE and TCE used as solvents were dried over molecular sieves prior to use. Triethylamine was freshly distilled just prior to use (bp 89°C).

DISCUSSION

The object of this work is to show how light-sensitive polymers change their spectral response and photosensitivity with changing chromophores in the original monomers. Thirty-five DVCP-type polyesters have been selected for inclusion in Table II to show the significant changes in the polymers with the use of various bisphenols. The 28 light-sensitive bisphenols of Table I were all

TABLE I
Light-Sensitive Bisphenols

Bisphenol	m.p., °C	λ_{max}, nm	Solvent
1. Disalicylalacetone or 2,2′-dihydroxydibenzalacetone	168	- - -	MeOH
2. 4,4′-Dihydroxydibenzalacetone	237–8	331	DCE
3. Bis(4-hydroxy-3-methoxybenzal)acetone, or divanillalacetone, or DVA	159–161	390	MeOH
4. Bis(4-hydroxy-3,5-dimethoxybenzal)acetone, or disyringalacetone, or DSA	157–160	392	MeOH
5. 2,5-Bis(2-hydroxybenzylidene)cyclopentanone, or D2CP	82–6	355	DMF
6. 2,5-Bis(3-hydroxybenzylidene)cyclopentanone, or D3CP	295–7	362	DMF
7. 2,5-Bis(4-hydroxybenzylidene)cyclopentanone, or D4CP	319–321	390	DMF
8. 2,5-Bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone or divanillalcyclopentanone, or DVCP	214–5	404 393	MeOH TCE
9. 2,5-Bis(4-hydroxy-3,5-dimethoxybenzylidene)cyclopentanone or disyringalcyclopentanone, or DSCP	240–3	425	MeOH
10. 2,5-Bis(3-bromo-4-hydroxy-5-methoxybenzylidene)cyclopentan-one, or bromo-DVCP	274–5	397	MeOH
11. 2,5-Bis(3-chloro-4-hydroxy-5-methoxybenzylidene)cyclopentan-one, or chloro-DVCP	278–9	397	DMF
12. 2,5-Bis(3-iodo-4-hydroxy-5-methoxybenzylidene)cyclopentan-one, or iodo-DVCP	253-4	389	DCE
13. 2,5-Bis(3-hydroxy-4-methoxybenzylidene)cyclopentanone or iso-DVCP	218–220	399	MeOH
14. 2,5-Bis(2-hydroxy-3-methoxybenzylidene)cyclopentanone or ortho-DVCP	114–8	333	DCE
15. 2,5-Bis(4-hydroxybenzylidene-3-sulfonic acid)cyclopentanone or sulfo-D4CP	—	388	DMF
16. 2,5-Bis(4-hydroxy-3-nitrobenzylidene)cyclopentanone or 3-nitro-D4CP	269–271	360	TCE
17. 2,5-Bis(2-hydroxy-3-nitrobenzylidene)cyclopentanone or 3-nitro-D2CP	255–8	340, 385	TCE
18. 2,5-Bis(2-hydroxy-5-nitrobenzylidene)cyclopentanone or 5-nitro-D2CP	248–250	371 336	TCE DMF
19. 2,5-Bis(5-hydroxy-2-nitrobenzylidene)cyclopentanone or 2-nitro-D5CP	235–7	300, 328	MeOH
20. 2,5-Bis(4-hydroxy-5-methoxy-3-nitrobenzylidene)cyclopentan-one or nitro-DVCP	280d	357	TCE
21. 2,5-Bis(4-hydroxy-3,5-di-t-butylbenzylidene)cyclopentanone or butyl-D4CP	110d	396	TCE
22. 2,6-Bis(2-hydroxybenzylidene)cyclohexanone, or disalicylalcyclohexanone, or D2CH	153	349	MeOH
23. 2,6-Bis(3-hydroxybenzylidene)cyclohexanone or D3CH	210–3	339	MeOH
24. 2,6-Bis(4-hydroxybenzylidene)cyclohexanone or D4CH	282–8	370	MeOH
25. 2,6-Bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone or DVCH	179	384 342	MeOH DCE
26. 2,6-Bis(4-hydroxy-3-methoxybenzylidene)4-methylcyclohexan-one or DVMCH	170–1	385	MeOH
27. 2,6-Bis(4-hydroxy-3-methoxybenzylidene)4-t-butylcyclohexan-one or DVBCH	201	380	MeOH
28. 4,4′-Dihydroxychalcone or DHC	201–4	334 348	DCE MeOH

prepared in our laboratories, but 1 and 2 were not available when this series of polyesters was run.

Although polyesters of DVCP have been prepared from acid chlorides Cl—

TABLE II
Polyesters from Light-Sensitive Bisphenols

Polymer	Bisphenol, mole-%	Acid chloride, Mole-%	η_{inh}	Solvent	Sensitivity value	λ_{max}, nm	Element	Analysis Calc'd, %	Fd, %
1.	DVCP, 100	sebacyl, 100	0.34	TCE	B*	366			
2.	DVCP, 65 TCIBPA, 35	sebacyl, 100	0.43	TCE	B	366			
3.	DVCP, 60 TCIBPA, 40	sebacyl, 100	1.09	TCE	E	363	Cl	10.8	10.8
4.	DVCP, 56 TCIBPA, 44	isophthaloyl, 100	0.56	DCE	C	363	Cl	12.0	14.6
5.	DVCP, 56 TCIBPA, 44	isophthaloyl, 50 azelaoyl, 50	1.52	DCE	E	366	Cl	12.5	13.9
6.	DVCP, 56 TCIBPA, 44	isophthaloyl, 30 sebacyl, 70	0.75	DCE	E	366	Cl	12.1	13.3
7.	DVCP, 60 BPA, 40	isophthaloyl, 50 terephthaloyl, 50	1.18	TCE	D	—			
8.	DVA, 60 TCIBPA, 40	sebacyl, 100	1.16	DCE	E	347			
9.	DVCH, 50 TCIBPA, 50	sebacyl, 100	0.83	DCE	B	342	Cl	13.6	13.3
10.	DVMCH, 50 TCIBPA, 50	sebacyl, 100	1.29	DCE	B	343	Cl	13.2	13.5
11.	Bromo-DVCP, 60 TBrBPA, 40	sebacyl, 100	0.41	DCE	D	360	Br	32.4	31.4
12.	Chloro-DVCP, 60 BPA, 40	azelaoyl, 100	1.10	DCE	E	360	Cl	8.6	8.6
13.	Chloro-DVCP, 60 BPA, 40	sebacyl, 100	1.10	DCE	E	360 nm	Cl	8.3	8.0
14.	Chloro-DVCP, 60 TCIBPA, 40	sebacyl, 100	0.69	DCE	D	359	Cl	17.6	17.2
15.	Chloro-DVCP, 56 BPA, 44	azelaoyl, 50 isophthaloyl, 50	0.81	DCE	E	358	Cl	8.3	8.4
16.	Iodo-DVCP, 50 BPA, 50	sebacyl, 100	0.18	DCE	A	363	I	22.1	18.5
17.	Iodo-DVCP, 60 TCIBPA, 40	azelaoyl, 50 isophthaloyl, 50	0.78	DCE	E	360	Cl I	8.2 22.4	9.5 21.4

No.	Light-sensitive bisphenol / comonomer (code, mol %)	Acid chloride (code, mol %)	η_{inh}	Solvent	Sensitivity	λ_{max} (nm)	Cl/N		
	BPA, 50						Cl	13.4	12.9
19.	2-Nitro-D5CP, 49 / TClBPA, 51	sebacyl, 100	0.43	DCE	O	328	N	2.5	3.3
20.	3-Nitro-D2CP, 50 / BPA, 50	sebacyl, 100	0.33	DCE	B	333	N	2.9	3.1
21.	3-Nitro-D4CP, 54 / BPA, 46	sebacyl, 100	0.51	DCE	E	345	N	3.2	3.1
22.	5-Nitro-D2CP, 56 / BPA, 44	sebacyl, 100	0.23	DCE	A	336	N	3.2	3.4
23.	D2CP, 56 / TClBPA, 44	sebacyl, 100	—	DCE	O	272			
24.	D3CP, 56 / TClBPA, 44	sebacyl, 100	0.37	TCE	B	329			
25.	D4CP, 50 / TClBPA, 50	sebacyl, 100	0.35	TCE	C	355	Cl	14.3	15.6
26.	Ortho-DVCP, 60 / TClBPA, 40	sebacyl, 100	0.25	DCE	O	318	Cl	10.8	12.7
27.	Iso-DVCP, 56 / TClBPA, 44	sebacyl, 50 / isophthaloyl, 50	0.31	TCE	B	376			
28.	Butyl-D4CP, 56 / TClBPA, 44	azelaoyl, 100	0.06	DMF	A	378			
29.	DSCP, 50 / TClBPA, 50	sebacyl, 100	0.40	DCE	C	370	Cl	12.8	14.7
30.	Sulfo-D4CP, 56 / TClBPA, 44	1,9-bischloroform-yloxynonane, 100	0.29	DMF	B	342			
31.	D2CH, 50 / TClBPA, 50	sebacyl, 100	0.27	DCE	O	344	Cl	14.1	19.0
32.	D3CH, 50 / TClBPA, 50	sebacyl, 100	0.36	DCE	A	325	Cl	14.1	15.1
33.	D4CH, 50 / TClBPA, 50	sebacyl, 100	1.21	DCE	A	331	Cl	14.1	14.8
34.	DVBCH, 50 / TClBPA, 50	sebacyl, 100	0.68	DCE	B	345	Cl	12.7	13.4
35.	DHC, 65 / TClBPA, 50	sebacyl, 100		DCE	B	315	Cl	11.0	10.9

(1) Light-sensitive bisphenol codes explained in Table I. (2) Nonlight-sensitive bisphenols: BPA = bisphenol A, TClBPA = tetrachlorobisphenol A, TBrBPA = tetrabromobisphenol A. (3) Inherent viscosities in indicated solvent, calculated in dl/g (0.25 g/100 ml at 25°C). (4) Solvents used: DCE = 1,2-dichloroethane; TCE = 1,1,2-trichloroethane; DMF = N,N-dimethylformamide. (5) Sensitivity values calculated as described in text. (6) UV absorption run in solution on Cary Model 15 spectrophotometer. (7) Polymer 30 was run interfacially with the C-9 bischloroformate instead of an acid chloride.

TABLE III
Absorption Maxima of DVCP-Type Bisphenols and of Polyesters Prepared from Them. Photosensitivity of the Polyesters[a]

1. Polyesters from Bisphenols Made from Vanillin and Various Ketones

	Polymer 3	8	10	9	35	34
Bisphenol	DVCP	DVA	DVMCH	DVCH	DHC	DVBCH
Abs. max.	404 nm	390 nm	385 nm	384 nm	348 nm	380 nm
SolventMH	MH	MeH	MH	MH	MH	MH
Polym. abs. max.	363 nm	347 nm	343 nm	342 nm	315 nm	345 nm
Polym. sensitivity	E	E	B	B	B	B
Ketone	cyclopentanone	acetone	4-methylcyclohexanone	cyclohexanone	chalcone	4-t-butylcyclohexanone

2. Use of Isomeric Hydroxybenzylidene Compounds

	Polymer 23	24	25	31	32	33
Bisphenol	D2CP	D3CP	D4CP	D2CH	D3CH	D4CH
Abs. max.	355 nm	362 nm	390 nm	349 nm	339 nm	370 nm
Solvent	DMF	DMF	DMF	MeOH	MeOH	MeOH
Polym. abs. max.	272 nm	329 nm	355 nm	344 nm	325 nm	331 nm
Polym. sensitivity	0	B	C	0	A	A

3. Effect of Methoxyl Groups on the Bisphenol

	Polymer 25	3	29	33	35
Bisphenol	D4CP	DVCP	DSCP	D4CH	DHC
Abs. max.	390 nm	404 nm	425 nm	370 nm	348 nm
Solvent	DMF	MeOH	MeOH	MeOH	MeOH
Polym. abs. max.	355 nm	363 nm	370 nm	331 nm	315 nm
Polym. sensitivity	C	E	C	A	B
Methoxyls	0	2	4	0	

4. Halogen Substitution on the DVCP Monomer

	Polymer 3	12	11	16
Bisphenol	DVCP	Chloro-DVCP	Bromo-DVCP	Iodo-DVCP
Abs. max.	404 nm	397 nm	397 nm	389 nm
Solvent	MeOH	DMF	MeOH	DCE
Polym. abs. Max.	363 nm	360 nm	360 nm	363 nm
Polym. sensitivity	E	E	D	A

5. Nitro Substituents on the Bisphenol

	18	19	26	21	22
Bisphenol	nitro-DVCP	2-nitro-D5CP	3-nitro-D2CP	3-nitro-D4CP	5-nitro-D2CO
Abs. max.	357 nm	328 nm	340, 385 nm	360 nm	371 nm
Solvent	TCE	MeOH	TCE	TCE	TCE
Polym. abs. max.	355 nm	328 nm	333 nm	348 nm	336 nm
Polym. sensitivity	B	0	B	E	A

(Polymer 18)

6. Isomers of DVCP

	3	26	27
Bisphenol	DVCP	Ortho-DVCP	Iso-DVCP
Abs. max.	393, 404 nm	333 nm	376 nm
Solvent	TCE MeOH	TCE	MeOH
Polym. abs. max.	363 nm	318 nm	376 nm
Polym. sensitivity	E	0	B

(Polymer 3)

7. Effect of 3,5-Di-t-butyl Substitution

	25	28
Bisphenol	D4CP	butyl-D4CP
Abs. max.	390 nm	396 nm
Solvent	DMF	TCE
Polym. abs. max.	355 nm	378 nm
Polym. sensitivity	C	A

(Polymer 25)

8. Effect of Substitution at the 4-Position of the Cyclohexanone Ring

	9	10	34
Bisphenol	DVCH	DVMCH	DVBCH
Abs. max.	384 nm	385 nm	380 nm
Solvent	MeOH	MeOH	MeOH
Polym. abs. max.	342 nm	343 nm	345 nm
Polym. sensitivity	B	B	B
4-Substituent	H	—CH$_3$	—C—(CH$_3$)$_3$

(Polymer 9)

CO—(CH$_2$)$_n$—CO—Cl in which n = 2, 3, 4, 5, 6, 7, 8, 11, 12, and 13, in this work only those from azelaoyl chloride (n = 7), sebacyl chloride (n = 8), isophthaloyl chloride, and terephthaloyl chloride are reported. Those from acid chlorides where n < 6 were soluble only in tetrachloroethane and did not build up to high molecular weight. Those where n > 8 are very soluble and of high molecular weight, but they are soft and somewhat rubbery.

In addition to the polycarbonates of reference 1, prepared interfacially, we have prepared polycarbonates of DVCP by high-speed interfacial condensation and in solution with 1,9-bischloroformyloxynonane, 1,10-bischloroformyloxy-decane, and 1,3,-bischloroformyloxy-2,2-dimethylpropane. With respect to photosensitivity and solubility, these polycarbonates resemble the azelates and sebacates.

The solubility of polyesters from DVCP in DCE is improved if 40–50 mole-% of the DVCP is replaced with bisphenol A, tetrachlorobisphenol A, or tetrabromobisphenol A. This does not significantly reduce the photosensitivity of the polyesters. These nonlight-sensitive bisphenols were used in the preparation of all the polyesters of Table II except for polymers 1 and 35.

The polyazelates and polysebacates of DVCP-type bisphenols generally form long, tough, yellow fibers. Those with isophthaloyl chloride are usually formed as beads which are quite soluble in DCE. Those with terephthaloyl chloride are much harder and also somewhat less soluble in DCE.

Attempts to prepare polyesters in solution from Sulfo-D4CP were not successful, but a polycarbonate (30) was prepared by high-speed interfacial condensation with 1,9-bischloroformyloxynonane.

As the various light-sensitive bisphenols were prepared, polyesters were made from them and the photosensitivity and absorption maxima of the polyesters were compared.

Although the properties of the monomers are shown in Table I and those of the polymers in Table II, the summary of this report groups them for comparison of specific structural changes in the chromophore (Table III).

SUMMARY

The experimental data shown in Tables I and II enable us to compare the polyesters prepared from various light-sensitive bisphenols. In the data listed below, structural and conformational variations in the monomers may be compared with the effects on polyesters prepared from these monomers. When comparing the spectral data, it must be understood that in polar solvents such as methanol and dimethylformamide, there is some ionization of the phenol to phenolate with a considerable bathochromic shift. With DVCP, the peak absorption is 393 nm in TCE and 404 nm in MeOH. It is preferable to compare data run in the same solvent. Unfortunately, some of the monomers and polymers have limited solubility, and data for runs in the various solvents are not available. Most of the polymer spectra were run in the chlorinated solvents DCE and TCE.

The sensitivity values vary with molecular weight of the polymer and with the mole fraction of chromophore present. The data presented here must be considered qualitative. But it is sufficient to determine that two polymers with approximately equal amounts of two different bisphenols and with similar in-

herent viscosities which show sensitivity values represented by B and C are of significantly different sensitivities. The important sensitivity value is found when polymers are coated and exposed in actual conditions, i.e., a lithographic plate exposed to a particular light source and developed with a particular solvent system; or a photoresist from one of the polymers coated, exposed, and developed under quite different conditions.

Using the data obtained and shown above, it may be concluded: (1) DVCP is better for production of highly photosensitive polyesters than DVA, but both are effective; (2) 4-hydroxybenzylidene compounds are better than 3-hydroxy compounds; 2-hydroxy compounds do not produce photocrosslinkable polymers; (3) the addition of methoxyls is advantageous; (4) halogen substitution on the DVCP greatly increases the molecular weight of the bisphenol but does not significantly alter the absorption or photosensitivity of the polyesters; chloro and bromo substitution is preferable to iodo substitution; there is no apparent sensitization of the polymer by halogens on the DVCP; (5) nitro substituents generally cause densensitization; (6) DVCP is much better than *ortho*-DVCP or *iso*-DVCP as a polymer intermediate; (7) although 3,5-di-*t*-butyl substitution causes a bathochromic shift in absorption, it prevents build-up to a polymer of high molecular weight; (8) substitution at the 4-position in the cyclohexanone ring does not produce bisphenols whose polyesters are better than those from DVCP.

Table III summarizes the comparative data for the polymers. The sections are numbered as in the preceding paragraph. The individual polymers are numbered as in Table II where their composition, sensitometry, and analyses may be found. The structure and physical properties of the light-sensitive bisphenols used in preparing the polymers are shown in Table I, using the abbreviations shown there, as DVCP, DVA, etc.

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