

# UV-Sensitive Polyarylates as Photolithographic Emulsions

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## SYNOPSIS

Several UV-sensitive polyarylates based on bisbenzylideneketones for use as potential photolithographic emulsions were obtained by interfacial polycondensation. The structures of obtained UV-sensitive monomers and polymers were confirmed by infrared, <sup>1</sup>H-NMR, and UV spectroscopies. Mechanical and dielectric properties of the obtained polyarylates (including dielectric loss factor, dielectric constant, volume and surface resistivity, and dielectric strength) were evaluated. The investigations show that some of the new polymers obtained in this study may find application as photoresists. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

For several years, our group has conducted photopolymer research.<sup>1-5</sup> Polyesters (polyarylates and polysulfonates) with photosensitive properties were obtained as copolymers, including chlorobisphenols, bisphenol A (BA), and the UV-sensitive bisphenol (SB) -bis(3-ethoxy-4-hydroxybenzylidene)acetone. However, our previous investigations<sup>6</sup> did not include the broad subject of polyarylates nor address the influence of substrate on the photosensitive properties of polymers.<sup>1</sup> These subjects are presented here. The objective of the present work is thus the synthesis of UV-sensitive polyarylates based on UV-sensitive bisbenzylideneketones and the determination of properties of the resulting polymers with interest in the bisphenols structure and side chains in bisphenol aromatic rings. Because polyarylates could have applications in electronics (i.e., in integrated circuit production using the photolithographic process), we investigated dielectric properties, among them the dielectric loss factor, dielectric constant, volume and surface resistivity, and dielectric strength.

Photopolymers are high-molecular-weight compounds containing photosensitive groups that via electron excitation result in macroradicals. The photosensitive groups can undergo macromolecular crosslinking or degradation reactions. Some units

that find application as photocrosslinking polymers are presented in Table I.<sup>7</sup>

## EXPERIMENTAL METHODS

### Monomer (Bisphenols) Synthesis

For interfacial polycondensation reactions, we used several photosensitive bisphenols of the general formula presented in Figure 1.

The obtained photopolymers have a negative character [Fig. 1(a-f)]. A degradation of the N—N bond may occur, giving polymers with a positive character [Fig. 1(g)]. Photosensitive bisphenols synthesis (i.e., the synthesis of bisphenols that have a dibenzylideneketone system) is carried out in acid medium at 0–2°C. The reaction is an aldol condensation between an aldehyde, which has no hydrogen atom in the  $\alpha$  position, and a ketone (Claisen-Schmidt reaction).<sup>8,9</sup> In this reaction, the protonated carbonyl group from the aldehyde is attached to the  $\alpha$  carbon of the keton-enol form, giving an unstable addition product. In acid medium, dehydration quickly occurs, leading to an  $\alpha,\beta$ -unsaturated compound. Azines were obtained by reaction of hydrazine with carbonyl group, with concurrent water molecule elimination.

### Polymers Synthesis

Via interfacial polycondensation from the photosensitive bisphenols and bisphenol A, copolyarylates

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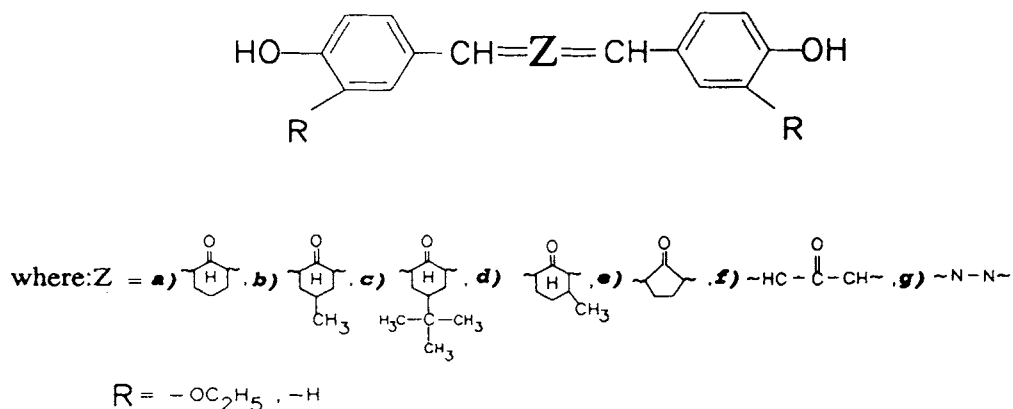
**Table I** Examples of Units Able to Undergo Photocrosslinking Reactions

Polymeric Unit	Formula	Polymer
Benzylideneacetophenone		Vinyl
Cinnamate		Vinyl
Styrylacrylate		Vinyl
Cinnamylidenemalonate		Polyester
<i>p</i> -Carboxycinnamate		Polyester
<i>p</i> -Phenylenebisacrylate		Polyester
		Vinyl

can be obtained. The elaborate conditions used are as follows.<sup>10,11</sup> The polycondensation reaction was carried out in a 250-ml three-neck flask with mechanical stirrer, dropping funnel, and thermometer. The water phase was bisphenols in alkali solution

and catalyst. As a catalyst, we used TEBA<sup>+</sup>Cl<sup>-</sup> chloride (triethylbenzylammonia chloride) 5 mol % relative to the bisphenol concentration.

The reaction was carried out in the temperature range of 20 ± 2°C. The time of addition of acid chlo-

**Figure 1** Formula scheme of photosensitive bisphenols.

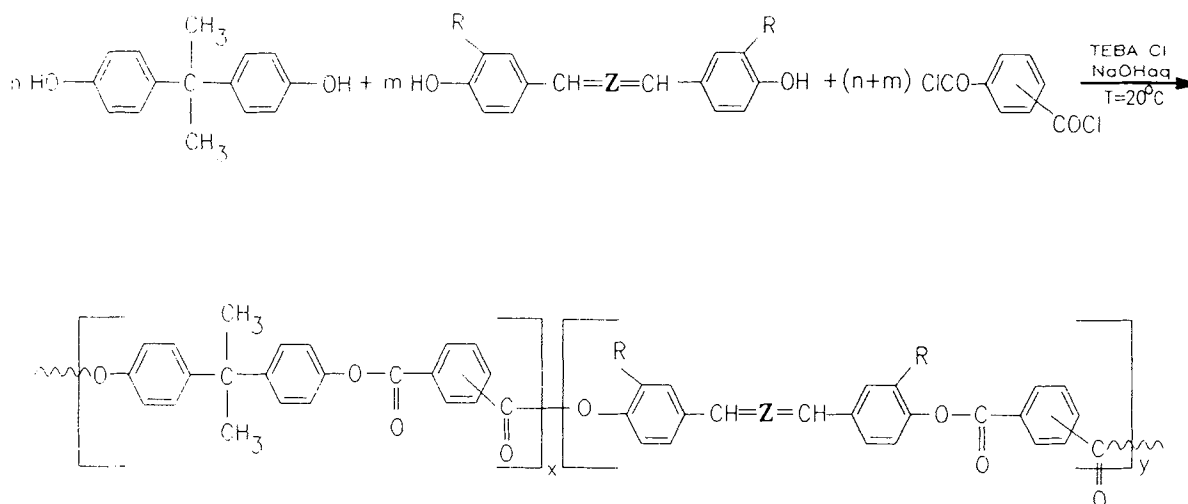


Figure 2 Polyarylate synthesis scheme (Z and R are defined in Fig. 1).

ride mixtures in methylene chloride (organic phase) was 5 min. The mixture of terephthalic and isophthalic acid chlorides was used in an optimal ratio 2 : 1.<sup>12,13</sup> After 2 h of stirring at a rate of about 1500 rpm, additional methylene chloride was added to dilute the reaction mixture. After another hour of stirring, the whole system was acidified. The organic phase was then separated, washed with distilled water, and dripped into acetone while intensive mixing was maintained. The polymer, which precipitated in acetone, was filtered, washed with acetone, and dried first under normal atmospheric pressure and then in a vacuum dryer at 70°C. A schematic representation of polyarylate synthesis is given in Fig. 2.

## Polymer Investigation Methods

### Preparation of Polymer Films

Polyarylate films were obtained by pouring a polymer solution in chlorinated hydrocarbon solvents onto a leveled glass plate held in a metal frame. The concentration of the solution was 8 g polymer/100 cm<sup>3</sup> solvent. This plate was kept undisturbed for 1 day and then dried 2.5 h at 60°C.

Infrared (IR) spectra were recorded from 700 to 4000 cm<sup>-1</sup> on a Specord IR-75 "Carl Zeiss" with KBr pellets (2 mg/300g KBr). The polymer tensile strength was measured according to the Polish standard.<sup>14</sup> We used 10 × 1-cm polymer film pieces, which were tensile through the longer side. Tensile strength is giving by eq (1):

$$\sigma = \frac{F_{\max}}{A_0} \quad (1)$$

where  $F_{\max}$  is the maximum tensile force [N] and  $A_0$  is the cross-sectional area [m<sup>2</sup>].

UV-vis spectra were recorded with a Perkin-Elmer Lambda2 spectrophotometer from 190 to 600 nm. The intrinsic viscosity was determined by an Ostwald viscosimeter. For dielectric loss factor, dielectric constant, and volume resistivity measurement, 5 × 5-cm polymer film pieces were used, for surface resistivity, 10 × 10 cm, and for dielectric strength, 20 × 5 cm.

The measurement of the dielectric loss factor was made in the frequency from 8 × 10<sup>1</sup> to 3 × 10<sup>5</sup> Hz with a scheering bridge made by Rohde-Schwarz (Germany) according to Polish standards.<sup>14</sup> In dielectric loss factor measurements, each sample had evaporated in high vacuum (5 × 10<sup>-5</sup> Torr) double-sided silver electrodes (rollers with 35 mm diameter). The temperature was changed in the range of 20–180°C, and dielectric loss factor was measured in 20, 40, 60, 80, 100, 120, 130, 140, 150, 160, 170, and 180°C for 80 Hz, 1 kHz, and 10 kHz. The variability of the characteristic frequency at 25°C was also checked and measured at 1, 5, 10, 50, 100, 200, and 300 kHz. The value of the dielectric loss factor was calculated from eq (2):

$$tg\delta = A*B*f \quad (2)$$

where  $A$  is the scale readout device,  $B$  is the frequency factor, and  $f$  is the frequency in kHz.

**Table II** Composition of Copolyarylates with Maximum SB Content

Polymer	Minimum BA Amount (mol %)	Maximum Photosensitive Bisphenol Amount (mol %)	Form of Polymer in Organic Phase	Capacity (%)
PAr0	100	0	Soluble	91
PAr1	33	67	Slightly soluble	80
PAr2	85	15	Swelling	81
PAr3	0	100	Highly swelling	86
PAr4	90	10	Swelling	79
PAr5	33	67	Slightly swelling	80
PAr6	33	67	Slightly swelling	81
PAr7	33	67	Slightly swelling	76
PAr8	33	67	Soluble	83
PAr9	75	25	Soluble	77

Structure of copolyarylates is given in Table VII.

Dielectric constant measurements of polymer layer films were made concurrently with dielectric loss factor measurements in the frequency of 1 kHz and temperature of 20–180°C. Because this value is rather constant in the whole range of temperature, we chose one for the temperature of 25°C, which is presented in Table VI.

The dielectric constant was calculated from eq. (3) and (4):

$$\epsilon = \frac{C}{C_0} \quad (3)$$

$$C_0 = \frac{S}{d} * 0.0885 \quad (4)$$

where  $S$  is the electrode area [cm<sup>2</sup>],  $d$  the distance between electrodes [mm],  $C$  the capacity [pF], and  $C_0$  the capacitance due to air [pF].

Volume resistivity was measured by a compensatory method according to the Polish standard<sup>14</sup> at 25°C. Volume resistivity was measured at free times and an average was taken. Volume resistivity was calculated from eq (5):

$$\rho_s = R_s \frac{S}{d} \quad (5)$$

where  $R_s$  is the sample through resistance,  $S$  is the electrode surface [cm<sup>2</sup>], and  $d$  is the sample thickness [cm].

Surface resistivity was measured at free times in temperature of 25°C and an average was taken. Surface resistivity was calculated from eq. (6):

$$\rho_p = \frac{2\pi}{R_p \ln \frac{D}{d}} \quad (6)$$

where  $R_p$  is sample superficial resistance [ $\Omega$ ],  $D$  is the inside diameter of outer electrode [cm], and  $d$  is the diameter of the inner electrode [cm].

The dielectric strength measurements were carried out by varying voltages at 25°C and a frequency of 1 kHz. Voltages were increased from zero up to breakdown voltage. The dielectric strength is given by eq (7):

$$U_p = \frac{U_{sk} \sqrt{2}}{d} \quad (7)$$

where  $U_{sk}$  is the root-mean-square value of critical voltage [kV] and  $d$  is the sample thickness [mm]

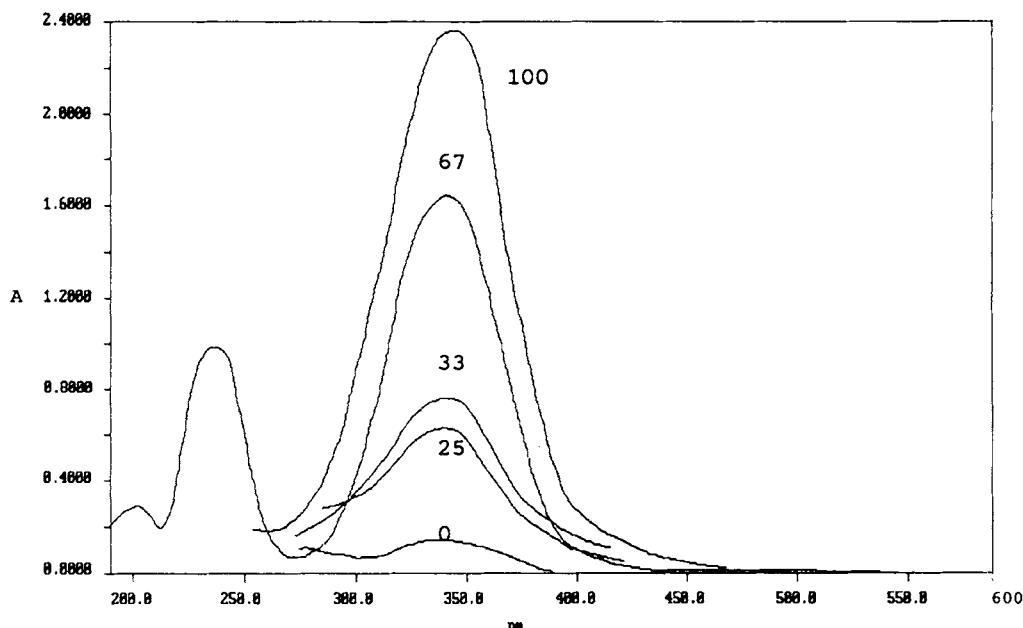
## RESULTS AND DISCUSSION

### Bisphenol Structures

Bisphenol structures were confirmed by spectral IR, proton-NMR, UV-vis spectra, and elemental analysis. The IR spectra of dibenzylidene ketones have a characteristic OH band (at 3400 cm<sup>-1</sup>), valence vibrations characteristic of a C=C—(C=O)—C=C group (1655 cm<sup>-1</sup>), and an asymmetrical valence vibration characteristic of a C—O—C group (1120–1280 cm<sup>-1</sup>).

Bisphenols have UV-vis absorption maxima in the range of 380–420 nm. This is attributable to a visible light absorption that stops down  $R$  band.

NMR spectra: bisphenol:

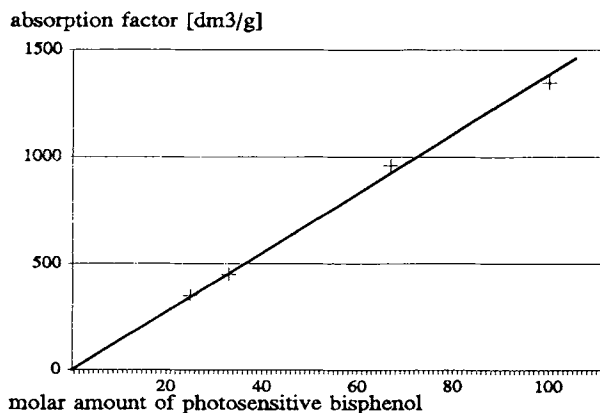


**Figure 3** UV-vis spectra for polymer series PAr3 with varying amounts of the photosensitive bisphenol. Values shown in mol % bisphenol.

- R = a, R<sub>1</sub> = —OC<sub>2</sub>H<sub>5</sub> (see Fig. 1).  $\delta = 1.45$  ppm (*t*, 6H, —CH<sub>2</sub>—CH<sub>3</sub>,  $J = 4.6$  Hz);  $\delta = 1.81$  ppm (*t*, 2H, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—,  $J = 4$  Hz);  $\delta = 2.91$  ppm (*t*, 4H, —CH<sub>2</sub>—C=CH,  $J = 4.6$  Hz);  $\delta = 4.15$  ppm (*q*, 4H, —OCH<sub>2</sub>CH<sub>3</sub>,  $J = 4.6$  Hz);  $\delta = 5.90$  ppm (*sd*, 2H, Ar—OH);  $\delta = 6.93$ – $6.98$  ppm, (m, 6H, benzene ring);  $\delta = 7.72$  ppm (*s*, 2H, =CH—).
- R = a, R<sub>1</sub> = —H (see Fig. 1).  $\delta = 1.77$  ppm (*t*, 2H, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—,  $J = 6$  Hz);  $\delta = 2.91$  ppm (*t*, 4H, —CH<sub>2</sub>—C=CH,  $J = 6$  Hz);  $\delta = 6.89$ – $7.44$  ppm (2xd, 8H, benzene ring,  $J_1 = J_2 = 4.3$  Hz);  $\delta = 7.63$  ppm (*s*, 2H, —CH=);  $\delta = 8.90$  ppm, (*sd*, 2H, Ar—OH).
- R = b, R<sub>1</sub> = —OC<sub>2</sub>H<sub>5</sub> (see Fig. 1).  $\delta = 1.39$  ppm (*t*, 6H, —CH<sub>2</sub>CH<sub>3</sub>,  $J = 4.6$  Hz);  $\delta = 2.56$  ppm (*m*, 2H, —CH<sub>2</sub>, cyclohexanone ring, and H—C—CH<sub>3</sub>, cyclohexanone ring);  $\delta = 3.1$  ppm (*d*, 2H, —CH<sub>2</sub> cyclohexane ring,  $J = 2$  Hz);  $\delta = 4.16$  ppm (*q*, 4H, —OCH<sub>2</sub>CH<sub>3</sub>,  $J = 4.6$  Hz);  $\delta = 5.80$  ppm (*sd*, 2H, Ar—OH);  $\delta = 6.87$ – $7.10$  ppm (*m*, 6H, benzene ring);  $\delta = 7.62$  ppm, (*s*, 2H, Ar—CH=).
- R = c, R<sub>1</sub> = —OC<sub>2</sub>H<sub>5</sub> (see Fig. 1).  $\delta = 0.92$  ppm (*s*, 9H, *tert*-butyl group, —CH<sub>3</sub>);  $\delta = 1.34$  ppm (*t*, 6H, —CH<sub>2</sub>—CH<sub>3</sub>,  $J = 6.8$  Hz);  $\delta = 2.40$  ppm (*m*, 1H, cyclohexanone ring);  $\delta = 3.01$  ppm (*d*, 2H, cyclohexanone ring);  $\delta = 3.36$  ppm (*s*, 2H, cyclohexanone ring);  $\delta = 4.07$  ppm (*q*, 4H, —CH<sub>2</sub>—CH<sub>3</sub>,  $J = 6.8$  Hz);  $\delta = 5.21$  ppm (*sd*, 2H, Ar—OH);  $\delta = 6.84$ – $7.09$  ppm (*m*, 6H, benzene ring);  $\delta = 7.52$  ppm (*s*, 2H, —CH=).

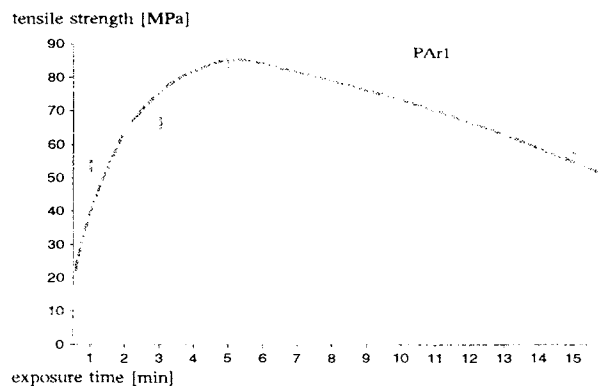
**Table III** Values of Absorption Factor  $\alpha$  for Polymers PAr3 with Differing Amounts of Photosensitive Bisphenols

Polymer	Molar % of Photosensitive Bisphenol	Concentration [g/dm <sup>3</sup> ]	Absorption Factor $\alpha$ [dm <sup>3</sup> /g]
PAr3	100	0.0177	1344
PAr3 (1)	67	0.0170	960
PAr3 (2)	33	0.0176	450
PAr3 (3)	25	0.0174	350



**Figure 4** Relationship between absorption factor and amount of PB 2,6-bis(3-ethoxy-4-hydroxybenzylidene)-cyclohexanone.

- $R = d$ ,  $R_1 = -H$  (see Fig. 1).  $\delta = 1.12$  ppm (d, 3H,  $-CH-CH_3$ );  $\delta = 2.97$  ppm (m, 3H, cyclohexanone ring);  $\delta = 6.87-7.16$  ppm (2xd, 4H, benzene ring,  $J_1 = J_2 = 4$  Hz);  $\delta = 7.60$  ppm (s, 2H,  $Ar-CH=$ );  $\delta = 8.2$  ppm (s, 2H,  $Ar-OH$ ).
- $R = e$ ,  $R_1 = -OC_2H_5$  (see Fig. 1).  $\delta = 1.35$  ppm (t, 6H,  $-CH_2-CH_3$ ,  $J = 3.5$  Hz);  $\delta = 3.03$  ppm (s, 4H,  $-CH_2-$ , cyclopentanone ring);  $\delta = 4.10$  ppm (q, 4H,  $-CH_2-CH_3$ ,  $J = 3.5$  Hz);  $\delta = 5.20$  ppm (sd, 2H,  $Ar-OH$ );  $\delta = 6.86-7.36$  ppm (m, 6H, benzene ring);  $\delta = 9.58$  ppm (s, 2H,  $-CH=$ ).
- $R = f$ ,  $R_1 = -OC_2H_5$  (see Fig. 1).  $\delta = 1.47$  ppm (t, 6H,  $-CH_2-CH_3$ ,  $J = 4.6$  Hz);  $\delta = 6.88-7.08$  ppm (m, 6H, benzene ring);  $\delta = 7.17$  ppm (d, 2H,  $Ar-CH=CH-$ ,  $J = 3$



**Figure 5** Tensile strength for PAr1 polymer as a function of exposure time.

Hz);  $\delta = 7.68$  ppm (d, 2H,  $Ar-CH=CH-$ ,  $J = 5$  Hz).

- $R = g$ ,  $R_1 = -H$  (see Fig. 1).  $\delta = 4.50$  ppm (sd, 2H,  $Ar-OH$ );  $\delta = 6.86-7.74$  ppm (2xd, 8H, benzene ring,  $J_1 = J_2 = 4$  Hz);  $\delta = 8.63$  ppm (s, 2H,  $-CH=$ ).
- $R = g$ ,  $R_1 = -OC_2H_5$  (see Fig. 1).  $\delta = 1.34$  ppm (t, 6H,  $-OCH_2-CH_3$ ,  $J = 6.8$  Hz);  $\delta = 4.06$  ppm (q, 4H,  $-OCH_2-CH_3$ ,  $J = 6.8$  Hz);  $\delta = 5.30$  ppm (sd, 2H,  $Ar-OH$ );  $\delta = 6.92-7.59$  ppm (m, 6H, benzene ring);  $\delta = 8.78$  ppm (s, 2H,  $-CH=$ ).

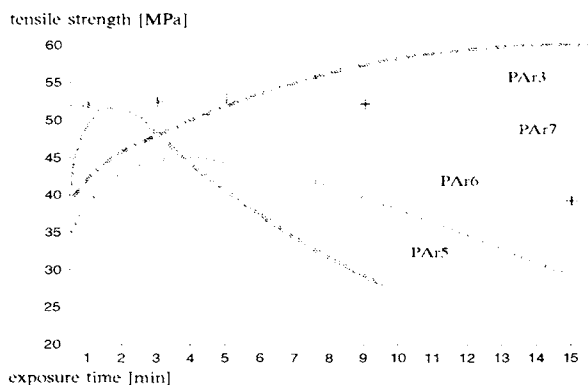
## Polymer Synthesis

### Bisphenols Ratio: BA and SB

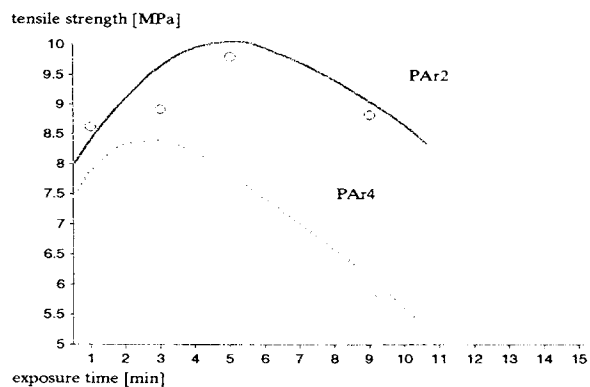
In the interfacial polycondensation, a mixture of bisphenols BA and SB were used. Their ratio was determined empirically. The amount of SB was decreased from 100% to the limiting quantity aimed at forming soluble polymer in the organic phase.

**Table IV** Mechanical Properties of Polyarylate Layers

Film Symbol	Average Thickness $d$ [ $\mu\text{m}$ ]	$F_{\text{max}}$ [N]	$A_0$ [ $\text{m}^2$ ]	$\sigma_{av}$ [ $\text{N}/\text{m}^2$ ] - [Pa]
PAr0	8.70	3.667	$8.7 \times 10^{-8}$	$4.21 \times 10^7$
PAr1	7.67	1.539	$7.7 \times 10^{-8}$	$1.99 \times 10^7$
PAr2	10.1	0.784	$10.1 \times 10^{-8}$	$7.76 \times 10^6$
PAr3	14.1	5.531	$14.1 \times 10^{-8}$	$3.92 \times 10^7$
PAr4	11.1	0.804	$11.1 \times 10^{-8}$	$7.24 \times 10^7$
PAr5	7.00	2.824	$7.0 \times 10^{-8}$	$4.03 \times 10^7$
PAr6	6.98	2.373	$6.9 \times 10^{-8}$	$3.44 \times 10^7$
PAr7	8.75	4.511	$8.8 \times 10^{-8}$	$5.12 \times 10^7$
PAr8	7.90	1.676	$7.9 \times 10^{-8}$	$2.12 \times 10^7$
PAr9	9.20	1.529	$9.2 \times 10^{-8}$	$1.66 \times 10^7$



**Figure 6** Tensile strength for PAr3, PAr5, PAr6, and PAr7 polymers as a function of exposure time.

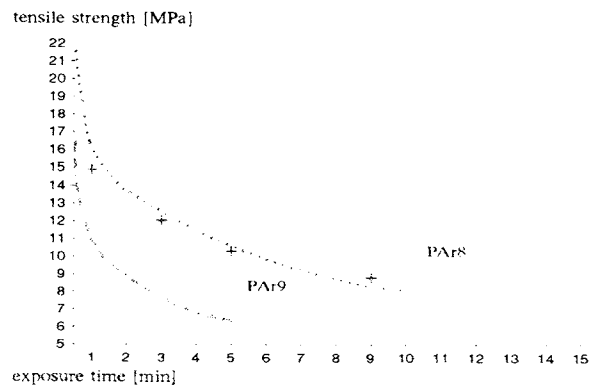


**Figure 7** Tensile strength for PAR2 and PAR4 polymers as a function of exposure time.

Polymers with high SB content would not dissolve in organic phase but instead precipitated during reaction. These polymers have very low molecular weights. Therefore, it was necessary to decrease the amount of SB to attain full solubility or possibly swelling of forming in organic phase polymer. The maximum amount of SB, the kind of polymer in the organic phase, and the capacity of the polycondensation reaction is given in Table II. Structures of the obtained polymers are given in Table VII.

#### Polyarylates (PAr) Solubility

Solubility measurements were carried out in chlorinated hydrocarbon solvents including 1,1,2-tetrachloroethane, chloroform, methylene chloride, carbon tetrachloride, and the nonchlorinated solvents toluene and cyclohexanone. The polymer powders were found to be insoluble in the latter two (nonchlorinated) solvents. In chlorinated solvents, the polymers first swell and then very slowly begin to solubilize. In each case, the best solvents follow: PAr(3,4,5,6,9) methylene chloride/tetrachloro-



**Figure 8** Tensile strength for PAR8 and PAR9 polymers as a function of exposure time.

**Table V** Intrinsic Viscosity of PAR0 to PAR9

Polymer	Intrinsic Viscosity $[\eta]$ [100 cm <sup>3</sup> /g]
PAr0	1.63
PAr1	1.29
PAr2	0.75
PAr3	0.99
PAr4	0.62
PAr5	1.13
PAr6	1.01
PAr7	1.38
PAr8	0.92
PAr9	0.59

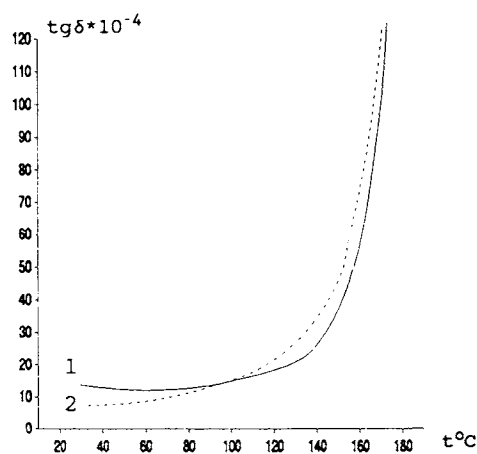
ethane (1 : 1 by volume), PAr(2,7,8) chloroform/tetrachloroethane (1 : 3 by volume), PAr1 tetrachloroethane. Some of the polymers, because of their high SB content, were insoluble in the chlorinated solvents mentioned above. To improve their solubility, the amount of SB was decreased until full solubility was attained. The amounts of SB for full soluble polymers are given in Table VII.

#### IR Analysis

IR spectra confirmed polyester structure with bis-benzylidene ketones groups. The 1750-cm<sup>-1</sup> band is characteristic of valence vibration of the C=O group in aromatic esters, and the 1670 cm<sup>-1</sup> band is the valence vibration of the C=O group conjugated with the C=C group.

#### UV-vis spectra

For all polymers, an absorption maximum in the wavelength range of 340–360 nm was observed,



**Figure 9**  $tg\delta$  polyarylate film (1) PAR1 and (2) PAR7 temperature dependence at 80 Hz.

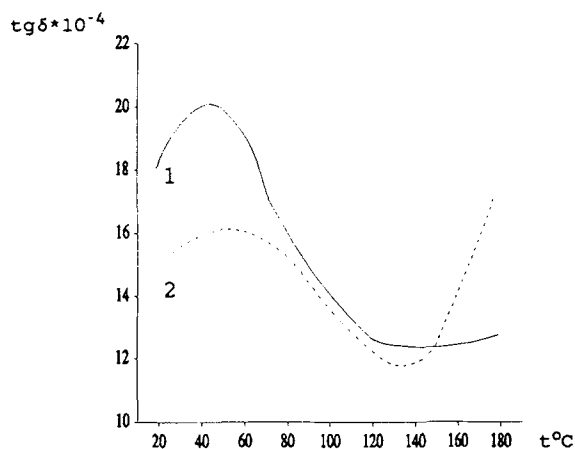


Figure 10  $tg\delta$  polyarylate film (1) PAR1 and (2) PAR7 temperature dependence at 1 kHz.

which indicates an  $n \rightarrow \Pi^*$  transition. Moreover, we found that in addition to increasing the amount of bisphenol in the mixture of the band, intensity at 350 nm is also increased as shown in Figure 3. This is attributed to the photosensitivity of bisphenol.

Because using molar absorption is not convenient, or simply not possible in the case of polymers, we determine the absorption factor  $\alpha$  [g/dm<sup>3</sup>] by eq (8):

$$\alpha = \frac{A}{c \cdot l} \tag{8}$$

where  $A$  is absorption [nm],  $c$  is the concentration [g/dm<sup>3</sup>], and  $l$  is the sample thickness [1 cm].

UV-vis investigations for polymers with differing amounts of SB 2,6-bis(3-ethoxy-4-hydroxybenzylidene)cyclohexanone were carried out. Calculated

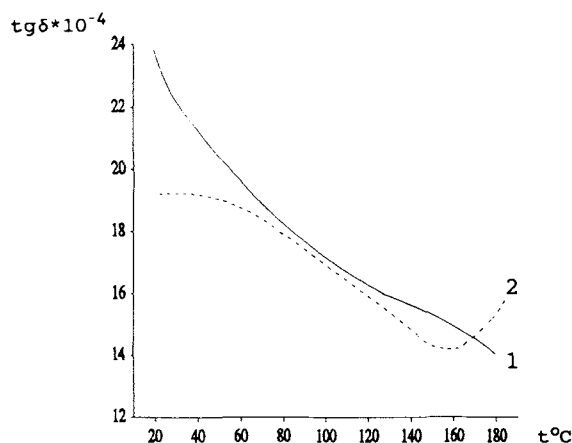


Figure 11  $tg\delta$  polyarylate film (1) PAR1 and (2) PAR7 temperature dependence at 10 kHz.

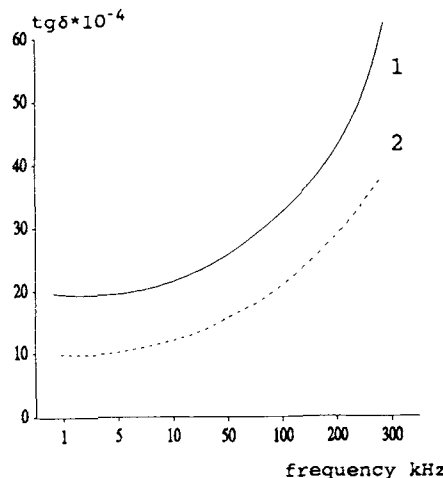


Figure 12  $tg\delta$  polyarylate film (1) PAR1 and (2) PAR7 frequency dependence at 25°C.

results and polymer concentrations are given in Table III.

Relationship between absorption factor and amount of SB 2,6-bis(3-ethoxy-4-hydroxybenzylidene)cyclohexanone in the PAR3 series is presented in Figure 4. From Figure 7, one can conclude that the absorption factor relationship for polymers with side-chain groups is proportional to the amount of SB in the bisphenols mixture.

**Mechanical Properties of Polymer Films**

The mechanical properties of polymer films (value of tensile strength) are given in Table IV [eq (1)]. Values of mechanical properties given in Table IV have comparative value only. As a standard, the PAR0 layer was selected, which was obtained from polyarylates synthesized on BA base.

**Crosslinking Ability**

Crosslinking effects were observed through investigating changes of mechanical properties (tensile strength). UV-vis crosslinking layers are expected

Table VI Values of Dielectric Properties for Polyarylate Layers PAR1 and PAR7 Measured at a Temperature of 25°C and a Frequency of 1 kHz

Measured Value	PAR1	PAR7
Dielectric constant $\epsilon$	1.9	2.1
$\rho_s$ [ $\Omega$ cm]	$5 \times 10^{17}$	$4.4 \times 10^{17}$
$\rho_p$ [ $\Omega$ ]	$1.6 \times 10^{12}$	$1.8 \times 10^{12}$
Dielectric strength [kV/mm]	103	106



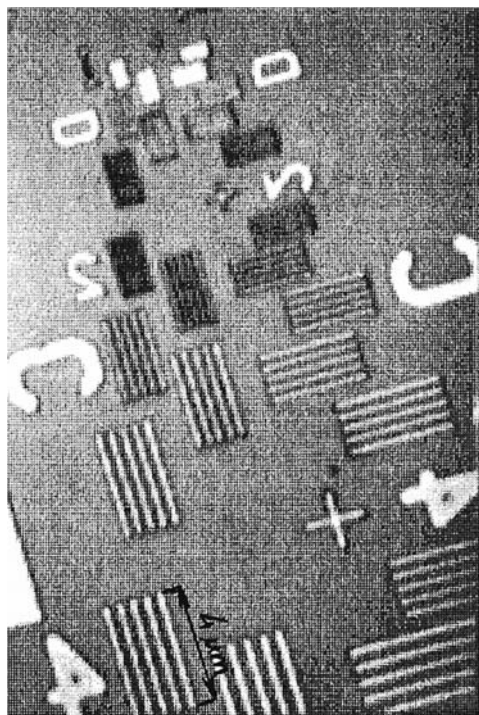
Table VII Structures of Obtained Polymers

Polymer	SB Amount (mol %)	Symbol
	0	PArO
	67	PAr1
	10	PAr2
	25	PAr3
	8	PAr4

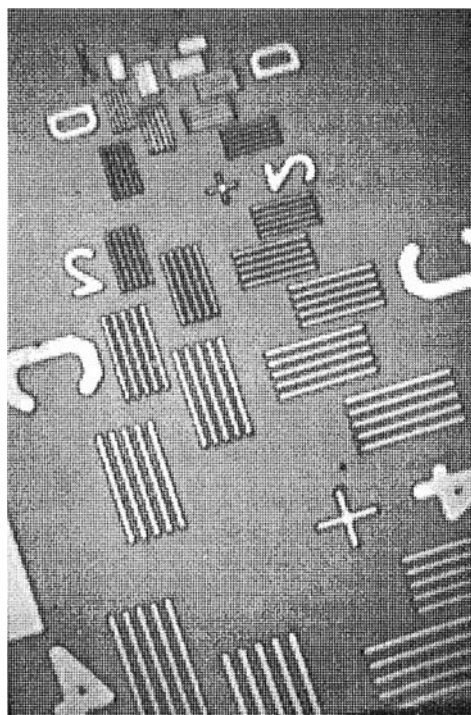
(Continued)

Table VII (Continued)

	67	PAR5
	67	PAR6
	33	PAR7
	33	PAR8
	20	PAR9



(1)



(2)

**Figure 13** Microscopic photographs obtained on Si/SiO<sub>2</sub> plates after exposure, development, and holding at temperature 130°C for 25 min. Polymers (1) PAR1 and (2) PAR7 are enlarged 200×.

to have higher values of tensile strength. Results are given in Figures 5–8.

#### **Determination of Intrinsic Viscosity**

Intrinsic viscosity (i.e., limiting viscosity number) was determined. In each case, obtained values were compared with the intrinsic viscosity of the polymer synthesised on BA base PAR0. These results are given in Table V.

#### **Dielectric Investigations**

Dielectric investigations were carried out for two selected polymer films PAR1 and PAR7. It must be stressed that results of these investigations have only comparative value. This is because the true layer properties are decreased due to, for example, dustiness. The influence of pollution on the electroinsulating properties of layers are particularly evident in dielectric constants, volume and surface resistivity, and dielectric strength measurements.

Dielectric loss factors were measured as a function of temperature at 80 Hz, 1 kHz, and 10 kHz. The

variability of the characteristic frequency at 25°C was also checked. Results are given in Figures 9–12.

Dielectric constant measurements were done concurrently with dielectric loss factor measurements. This is possible because the values are not altered in the range of investigated frequencies.  $\epsilon$  values are given in Table VI for 1 kHz and a temperature of 25°C. Table VI also shows dielectric loss factors, dielectric constants, volume  $\rho_s$ , surface  $\rho_p$  resistivity, and dielectric strength values.

For a better estimation of experimental measurements, preliminary application analysis of photoresists based on polyarylates PAR1 and PAR7 in UNITRA-CEMI electronic works was carried out. Microscopic photographs of these polymers are presented in Figure 13.

#### **Conclusions**

The solubility of a photosensitive polyarylate in organic phase depends on the photosensitive bisphenol structure. Bisphenols that have side chains in the 3 position of the aromatic ring exhibit better solubility

in the organic phase. The maximum solubility of bisphenols with side chains are at least three times higher than bisphenols without side chains. Only bisphenol M3 was unsuccessfully used to obtain a polyarylate that was not a copolymer with BA. The solubility of copolymers in chlorinated hydrocarbon solvents is poor due to the high amount of SB in the copolymer structure. For nonsoluble polymers, the amount of SB was decreased to the full solubility limit. The quality of obtained layers was poor. Only some gave transparent coats, which are very important in optical investigations. Several are mat or lightly mat, which prevents their application in optics but does not preclude their application in electronics.

PAR2, PAR4, and PAR9 layers have particularly low mechanical values. It is not possible to remove these layers from glass plates if their strength is below 85 kg/cm<sup>2</sup>. This layer tears and is not stable during storage. Most polymers exhibit increased mechanical properties after 1 to 5 min of exposure to UV light, with a maxima at  $t = 5$  min. Long-term exposure caused primarily photodegradation reactions. This observation is attributable to an excessive energy portion. The result is low polymer strength. PAR8 and PAR9 polymers are typical positive polymers; after exposure to UV light, their tensile strength decreases rapidly. Polymers with high molecular weight have side-chain groups in the aromatic rings. Some of the polymers contain high amounts of photosensitive bisphenol in their structure (up to 0.25 mol %), including PAR1, PAR3, PAR7, and PAR8. Polymers with low contents of photosensitive bisphenol obtained on *p*-hydroxybenzaldehyde base have lower values of intrinsic viscosity, including PAR2, PAR4, and PAR9. The investigated dielectric properties (dielectric loss factor, dielectric constant, volume and surface resistivity, and dielectric strength) suggest that these materials may be of use in photolithography. Photographs of pictures ob-

tained on Si/SiO<sub>2</sub> plates are clear and meet specifications of photosensitive layers using in industry.

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