

UV-SENSITIVE MODIFICATION OF POLYARYLATES

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Summary

Research has been carried out on UV-sensitive polyarylates from UV-sensitive and UV-insensitive bisphenols and phthaloyl chlorides. It has been found that the polyarylates have superior properties when bis(3-ethoxy-4-hydroxybenzylidene)acetone is used as the UV-sensitive bisphenol and bis(4-hydroxyphenyl)dichloroethylene is used as the UV-insensitive bisphenol. The main requirements for photoresists are fulfilled by the obtained UV-sensitive polyarylates.

1. Introduction

Polyarylates [1 - 4, 7] are linear polyesters; they consist of aromatic rings with ester groups between them in the main chain (Fig. 1). This structure determines the most important properties of the polyarylates: high glass-transition point, very good mechanical and dielectrical properties over a wide temperature range and excellent thermal and chemical resistance. Bisphenol

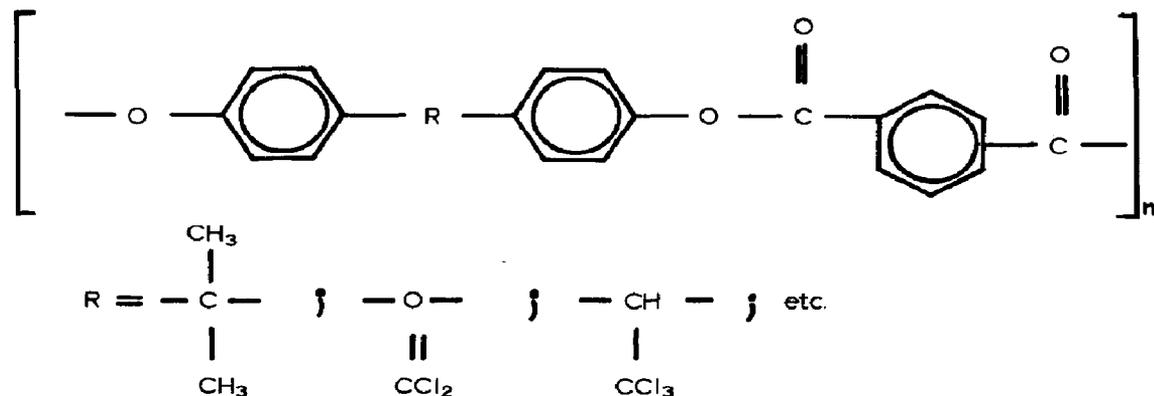


Fig. 1. Generalized structure for polyarylates.

A, chlorobisphenols and aromatic acid derivatives, *e.g.* chlorides, have mainly been used as the monomers. Polycondensation leading to the formation of polyarylates can be carried out in solution in chlorinated hydrocarbons; however, the most convenient method is the interfacial technique. The main advantages of employing interfacial polycondensation to obtain polyarylates are as follows.

(1) The rate of the reaction is fast and it can be carried out at room temperature and atmospheric pressure.

(2) There is the possibility of obtaining high molecular weight polymers and regulating their molecular weight.

(3) Monomers that are unstable at high temperatures may be used [10].

(4) Modification of the structure and properties of the polymers is easily achieved.

The first data on polyarylates were published by Eastman Kodak [5] in the U.S.A. and Gevaert [6] in Belgium. Polyarylates were obtained on the industrial scale in the U.S.A. and the U.S.S.R. [8] and on the preparative scale in the F.R.G. [2]. Research on chlorobisphenolic polyarylates has been carried out in the Technical University of Warsaw, Poland, since 1962.

The preparation and properties of polyarylates based on 2,2-bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane (chlorobisphenol I, CBP I) [9, 10] and aromatic acid chlorides has been described previously. The most useful are polyarylates based on 2,2-bis(*p*-hydroxyphenyl)-1,1-dichloroethylene (chlorobisphenol II, CBP II) [11 - 14]. Our findings on the mechanism of the interfacial synthesis of polyarylates [15] were noted by Morgan [16] to be important for future interfacial synthesis development. The main directions of research on chlorobisphenolic polyarylates are presented in Fig. 2.

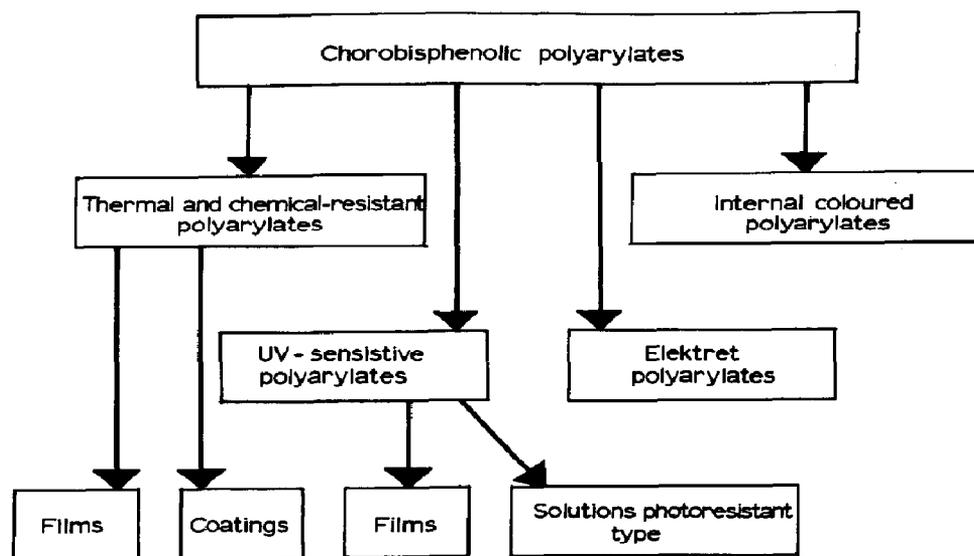
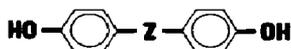


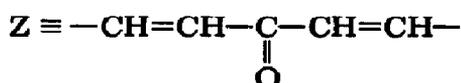
Fig. 2. Main directions of research on chlorobisphenolic polyarylates.

2. UV-sensitive bisphenols

The properties of UV-sensitive bisphenols are essentially determined by the chromophore system "Z" located between the aromatic rings.



A list of typical UV-sensitive (photo-cross-linkable) chromophores has been compiled by Williams *et al.* [17]. This list should be expanded to include the very interesting chromophore system for which



We have already published papers on polyarylates [18, 19]; in these studies, in addition to using such bisphenols as Bisphenol A and CBP II, bis(*p*-hydroxybenzylidene)acetone (BHBA) was used in the amounts 5.5, 10.0 and 16.6 mol.% as a UV-sensitive agent. Similar work on the application of a divinylbenzylidene structure with $-\text{OCH}_3$ groups on the aromatic rings in the synthesis of an aromatic polyester has been carried out by Borden [20]. Previously, we have carried out work on the application of compounds containing the divinylbenzylidene structure attached to the aromatic rings of the bisphenols by $-\text{OC}_2\text{H}_5-$ groups. The UV-sensitive bisphenol bis(3-ethoxy-4-hydroxybenzylidene)acetone (BEHBA) may be obtained, as well as BHBA, by a method given by Wittman [21]. The scheme is given in Fig. 3.

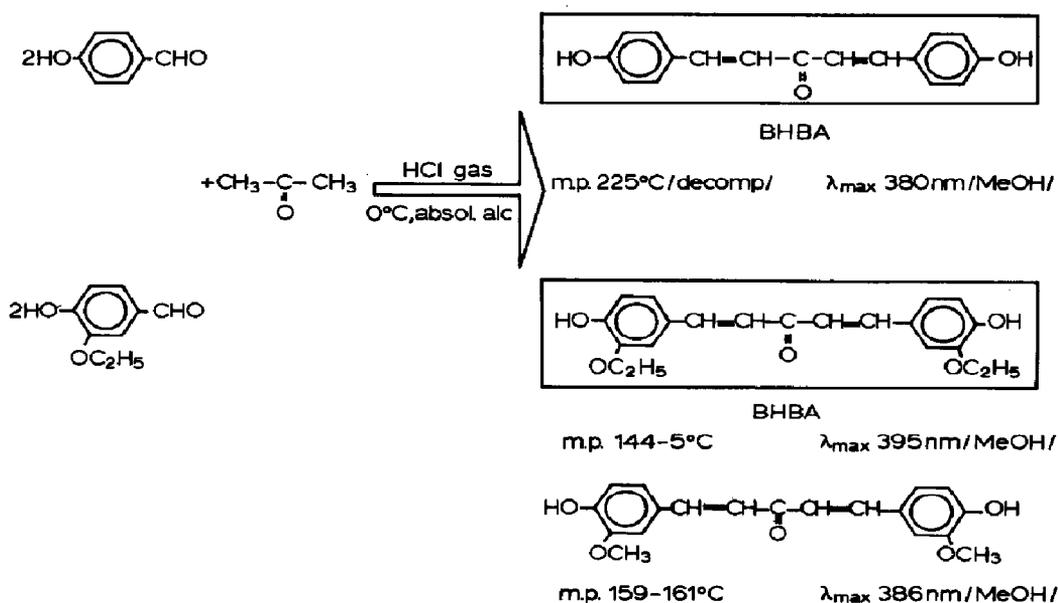


Fig. 3. Preparation of UV-sensitive bisphenols.

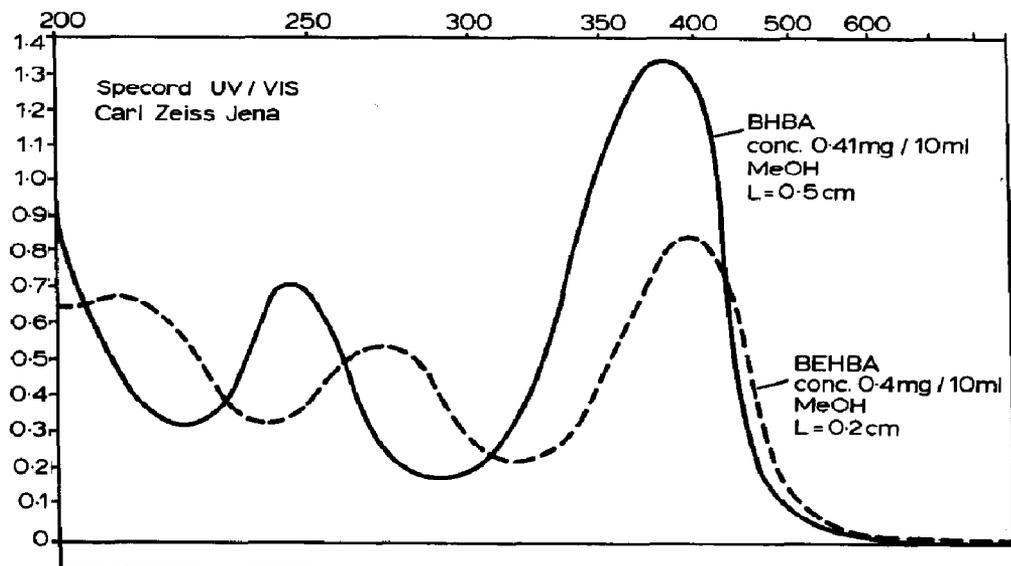
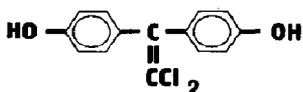


Fig. 4. UV-visible spectra of BHBA and BEHBA.

On the scheme the data on BEHBA are presented. For comparison there are data on bis(3-methoxy-4-hydroxybenzylidene)acetone (BMHBA) obtained by Borden [20]. The UV-visible spectra for BHBA and BEHBA are presented in Fig. 4. It should be pointed out that a favourable bathochromic effect is evident for BEHBA compared with both BHBA and BMHBA. The synthesis of BHBA and BEHBA is based on dissolving stoichiometric amounts of hydroxybenzaldehyde and acetone in absolute alcohol at 0 °C, and then passing gaseous HCl through the reaction mixture, causing the precipitation of glossy yellow crystals. After crystallization from nitrobenzene, bisphenols of the highest purity were obtained (yield, 95%). The purity was confirmed by spectroscopic analysis. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra obtained using Varian CFT-20 apparatus with deuterated acetone as the solvent are presented in Figs. 5 and 6. The high purity of the obtained bisphenols is evident from the clear and almost model character of the presented diagrams. This has an important influence on the properties of the polyarylates obtained from these bisphenols.

3. UV-insensitive bisphenols

The UV-insensitive bisphenols bis(*p*-hydroxyphenyl)propane and the useful and new CBP II were used [11].



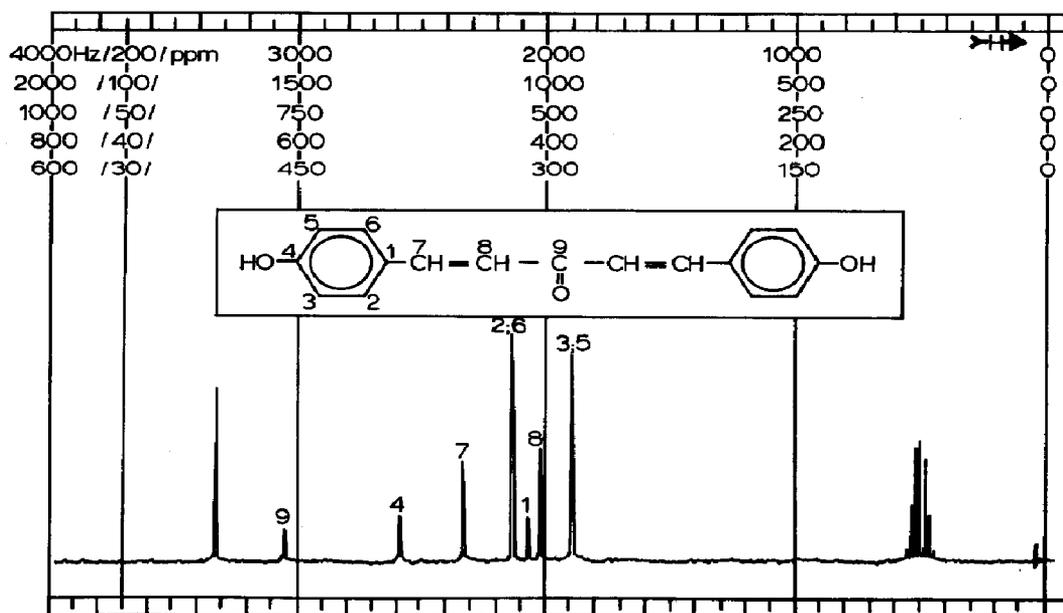


Fig. 5. ^{13}C NMR spectrum for BHBA.

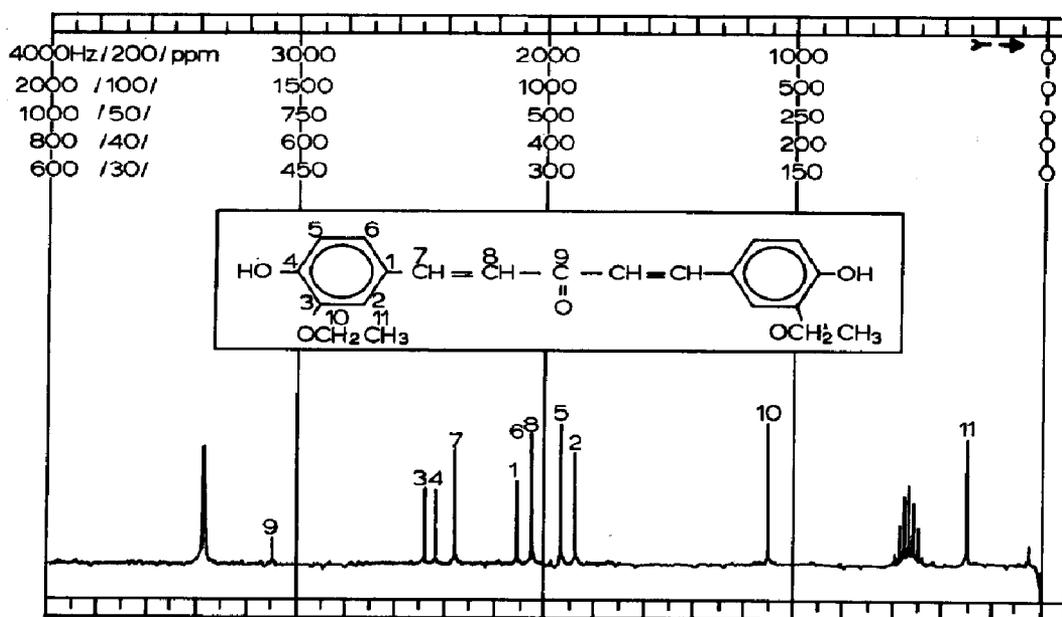


Fig. 6. ^{13}C NMR spectrum for BEHBA.

The structure of CBP II, in comparison with Bisphenol A, gives the polymer the following advantages: (i) there is an increase in thermal and chemical resistance; (ii) the temperature of the glass transition point is raised [37]; (iii) the inflammability is decreased; (iv) there is the possibility of thermal cross-linking at 200 °C.

The purity of the CBP II, as for UV-sensitive bisphenols, had a great influence on the properties of the polymers derived from it. The method given by McLaury *et al.* [22] to obtain very pure CBP II is very useful. According to McLaury, CBP II can be obtained by dehydrochlorination of CBP I in ammonia solution.

CBP II has already been employed to obtain polymers such as epoxy resins [23, 24], polycarbonates [25, 26], polysulphonates [27], polysulphones [28], polyurethanes [29] and other polymers [30, 31] as well as polyarylates [23, 27]. The importance of CBP II as monomer has increased in recent years owing to work done by the General Electric Company on the industrial method of obtaining the almost completely non-inflammable chlorobisphenolic polycarbonates [32 - 34].

4. Preparation of UV-sensitive polyarylates by an interfacial process

UV-sensitive polyarylates were obtained by interfacial polycondensation (Fig. 7) according to the method we have given in previous papers [18]. The aqueous alkali bisphenolic solution was the inorganic phase and the organic phase was a mixture of terephthalic and isophthalic acid chlorides in methylene chloride. The terephthaloyl and isophthaloyl chlorides were used in the ratio 2:1. This ratio has been found previously [11] to be optimal. The polycondensation reaction was carried out in interfacial conditions using triethylbenzylammonium chloride (TEBA) as the catalyst in the temperature range 20 ± 2 °C. The polymer precipitated from methanol was filtered, washed with methanol and dried first under normal atmospheric pressure and then in a vacuum dryer at 70 °C. The polymer thus prepared was examined. A number of syntheses using different molar ratios of sub-

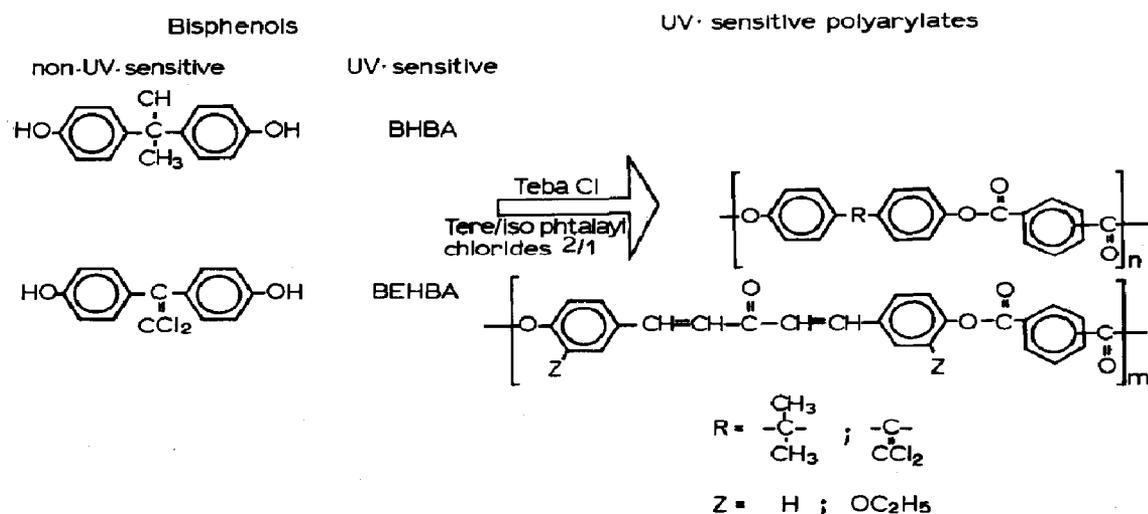


Fig. 7. Preparation of UV-sensitive polyarylates.

TABLE 1
Synthesis of polymers

Synthesis	Bisphenol		Concentration of UV-sensitive bisphenol (mol.%)	Yield (%)	Intrinsic viscosity ^a (100 ml g ⁻¹)
	UV-insensitive	UV-sensitive			
A1	BPA	BHBA	16.6	93	1.50
A2	BPA	BHBA	33.3	80 ^b	0.8 ^b
A3	BPA	BHBA	50.0	65 ^b	0.6 ^b
B1	BPA	BEHBA	16.6	97	1.42
B2	BPA	BEHBA	33.3	95	1.35
B3	BPA	BEHBA	50.0	95	1.30
C1	CBP	BEHBA	16.6	95	1.38
C2	CBP	BEHBA	33.3	93	1.31
C3	CBP	BEHBA	50.0	92	1.25

BPA, bisphenol A; CBP, 2,2-bis(*p*-hydroxyphenyl)-1,1-dichloroethylene; BHBA, bis(*p*-hydroxybenzylidene)acetone; BEHBA, bis(3-ethoxy-4-hydroxybenzylidene)acetone.

^aIn tetrachloroethane at 25 °C.

^bThere were difficulties in testing.

strates were carried out. Some of the results of these syntheses are presented in Table 1. In the syntheses where BHBA was used as the UV-sensitive bisphenol (series A) the yield of reaction in the cases where greater amounts of the bisphenol (syntheses A-2 and A-3) were used as well as the intrinsic viscosity were rather low because of the presence of numerous insoluble fractions. In the cases of syntheses based on BEHBA (series B and C) high and practically constant yields and intrinsic viscosities were obtained, independent of the amounts of BEHBA and the type of bisphenol, *i.e.* Bisphenol A (series B) or CBP (series C).

5. UV-visible spectra of UV-sensitive polyarylates

UV-visible spectra of the UV-sensitive polyarylates were recorded in dimethylene chloride using Carl Zeiss Specord UV-visible apparatus. UV-visible spectra are presented in Fig. 8 for an A-series polyarylate and in Fig. 9 for the the B-series polyarylates. The UV-visible spectra for the C-series polyarylates are basically similar to those of the B series. The shorter wavelength absorption band originates from the interaction between the aromatic ring and the double bond, involving electron transfer from the bonding π orbital to the non-bonding n orbital. The longer wavelength band originates from the presence of free non-bonding n electrons in the carbonyl groups and their transfer to the non-bonding n orbital. The $\pi \rightarrow \pi^*$ band at 242 nm is derived from the aromatic rings and is at the same wavelength for both A and B polyarylates. The $n \rightarrow \pi^*$ band is at 340 nm for A polyarylates

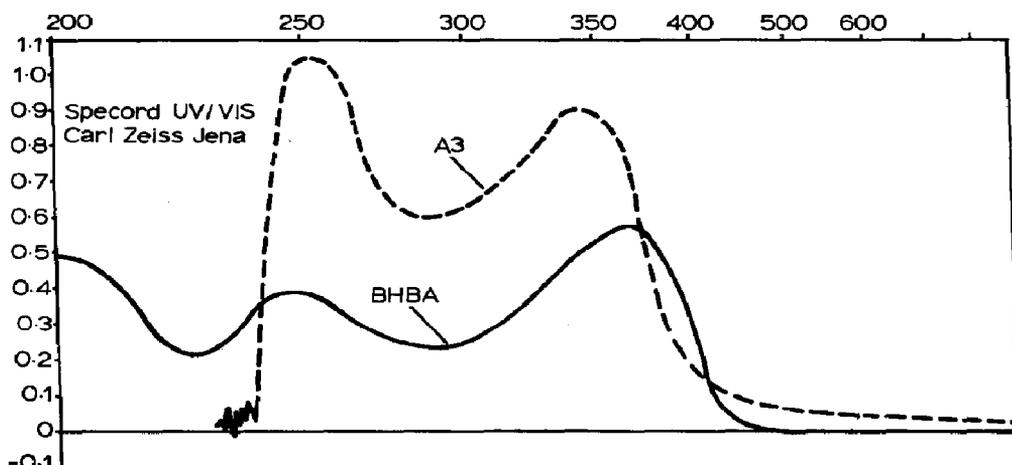


Fig. 8. UV-visible spectra of BHBA and polyarylate A3.

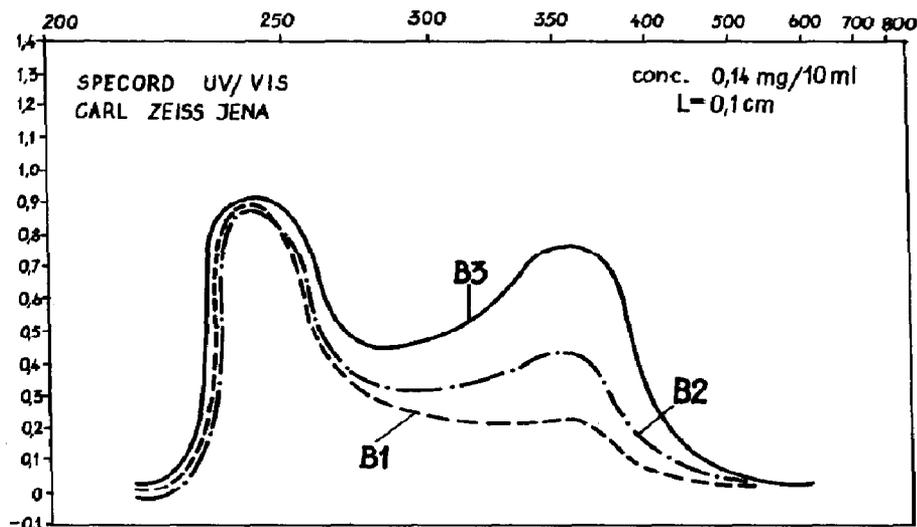


Fig. 9. UV-visible spectra of B-series polyarylates.

and 355 nm for B polyarylates. The bathochromic displacement of this band is connected with the presence of O-ethyl groups in the polymers obtained from BEHBA. The UV-visible spectra for A polyarylates and bisphenol BHBA are compared in Fig. 8.

The absorption of the BHBA $n \rightarrow \pi^*$ band was compared with the $n \rightarrow \pi^*$ band of the polymers: the absorption of the light-sensitive polyarylate is displaced from 360 to 335 nm, *i.e.* about 25 nm towards the shorter wavelengths. This displacement is due to the different auxochrome groups. OH groups of BHBA are exchanged for OR groups in the polyarylate macromolecule. The UV-visible spectra of the B-series polyarylates are presented in Fig. 9.

There is a direct connection between the intensity of the $n \rightarrow \pi^*$ band and the number of UV-sensitive groups in the polyarylate. It appears that

this band can be employed in the quantitative determination of UV-sensitive groups in such polymers.

6. Solubility of UV-sensitive polyarylates

The UV-sensitive polyarylates discussed here are very soluble in chlorinated hydrocarbons such as 1,1,2,2-tetrachloroethane, chloroform, chlorobenzene and methylene chloride, but are less soluble in *p*-xylene and dioxane. They are completely insoluble in alcohols and ketones. In general the choice of solvent for UV-sensitive polyarylates depends on the desired application. To prepare the UV-sensitive solution for photolithography it is necessary to have the correct solvent or mixture of solvents to spread over the semiconductor (Si + SiO₂) surface and/or the metallic surface (aluminium or copper). Such a solution must also have the right volatility. The best results were obtained using a mixture of chlorobenzene, 1,1,2,2-tetrachloroethane and dioxane in the ratio 3:1:1 (by volume). Even though 1,1,2,2-tetrachloroethane is the best solvent for polyarylates, its content in the mixture is not the highest. The properties of the 1,1,2,2-tetrachloroethane lead to a plastifying action since it does not completely evaporate from the layer during drying [35]. This is why chlorobenzene is better as the main solvent for UV-sensitive polyarylates. Dioxane is included in the mixture because of its volatility, this being important in the formation of the layer during rotation.

7. Photo-cross-linking of UV-sensitive polyarylate layers

UV-sensitive polyarylate layers were made by rotation at a rate of 3000 rev min⁻¹ while the 1% polymer solution was poured onto the semiconductor (Si + SiO₂) disks for 20 s. The thickness of the SiO₂ layers was about 2500 Å and the diameter of the disk was 1 in. After rotation the disks were dried at 70 °C for 20 min. These UV-sensitive layers had a thickness of 0.1 μm. It is possible to increase the thickness by increasing the molecular weight of the applied polymers, by increasing the concentration of the solution and by decreasing the speed and time of rotation. The dry polyarylate layers were then irradiated through a photomask in direct contact using a Carl Zeiss model 2119 source equipped with an HBO 200 W/2 lamp. The development process was carried out in 1,1,2,2-tetrachloroethane for 25 s. The disk was dried using a centrifuge (3000 rev min⁻¹, 1 min) and then vacuum dried under nitrogen at 100 °C for 40 min. The image was estimated, taking into account the quality of the frames. The estimations of obtained images are presented in Table 2. The resolution was estimated using an Olympus Tokyo microscope (magnification, 400X) equipped with an eyepiece to determine the size of the imaging details. The results of the adhesion

TABLE 2

Data for polyarylate layers

Syn-thesis	Bisphenol		Adhesion to metallic aluminium copper (Si + SiO ₂) according to PN-73/C-81531	Exposure time (s) for estimation of images		
	UV-insensitive	UV-sensitive		10	20	30
A1	BPA	BHBA	1	Poor	OK	Sharp
B1	BPA	BEHBA	1	OK	Sharp	Very sharp
B2	BPA	BEHBA	1	Sharp	Very sharp	Very sharp
B3	BPA	BEHBA	1	Sharp	Very sharp	Very sharp
C1	CBP	BEHBA	1	OK	Sharp	Sharp
C2	CBP	BEHBA	1	Sharp	Very sharp	Very sharp
C3	CBP	BEHBA	1	Very sharp	Very sharp	Very sharp

of UV-sensitive polyarylate layers to the metallic as well as to the semiconductor surfaces are presented in Table 2.

All types of coating adhered strongly to metals such as aluminium or copper and to semiconductors such as Si + SiO₂. Estimations of the qualities of the images are given in Table 2 and are, of course, relative. Coating polyarylates with a greater number of UV-sensitive groups led to a higher UV sensitivity. This type of dependence has been observed by other researchers [36]. The polyarylates of series B and C formed distinct images in shorter times of exposure than the polyarylates of series A. The increase in photosensitivity of B and C polyarylates originates from the presence of O-ethyl groups in the chromophore system (bisphenol BEHBA). This group exhibits a positive inductive effect and enriches the available electrons in the UV-sensitive groups. The degree of cross-linking for the same time of exposure was higher for BEHBA (B and C) polyarylates, giving a much more distinct image. The quantity of frames for all coatings is very good. The resolving power of the UV-sensitive polyarylate coating is very high and according to the Japanese Test No. 6 was determined as 1 - 2 μm , which is the equivalent of 400 lines mm^{-1} . Because of diffraction phenomena this resolution is the best possible result obtainable by applying such a technique. The topology obtained on the semiconductor plate using UV-sensitive C series polyarylates is presented in Fig. 10.

8. Conclusions

Four fundamental conclusions can be drawn from the research described above.

(I) The presented method of synthesis of UV-sensitive bisphenols allows one to obtain monomers of the highest purity which in turn has a significant influence on the properties of the polymers.

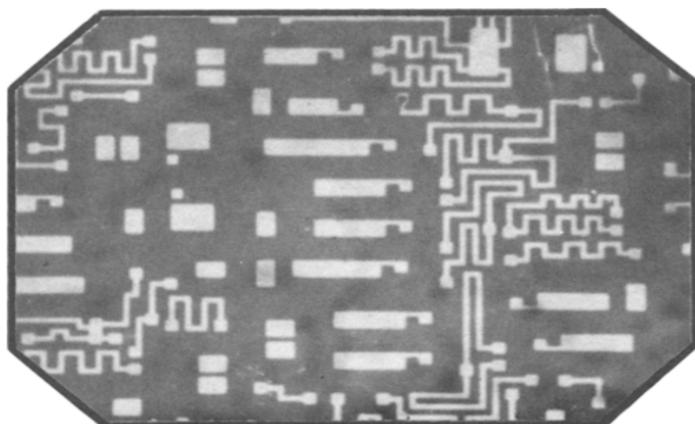


Fig. 10. Topology on the semiconductor plate using C-series polyarylates.

(II) The use of BEHBA instead of BHBA as a modification agent for the UV-sensitive polyarylates gives the following advantages: greater availability of raw materials (ethylvaniline from cellulosic liquors); better solubility of polymers; better yields of interfacial polycondensation; suitable bathochromic effect on the $n \rightarrow \pi^*$ band; better imaging results.

(III) Bisphenol A and CBP II can be used as UV-insensitive bisphenols. However, application of CBP II gives the possibility of additional thermal cross-linking by means of the $>C=CCl_2$ group, the consequences of this bonding being beneficial.

(IV) UV-sensitive polyarylates fulfil Williams' requirements [17] for photoresists: they dissolve in an appropriate solvent; they give homogenous coatings; the dried coatings have very good adhesion to the substrates; the photographic speed meets the processing time requirements for very thin layers; the image is very easily developed; the developed image withstands thermal and chemical treatment, although the resistance to etching agents is not yet satisfactory in each case; the image is easily stripped after thermal treatment.

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