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UV-SENSITIVE POLYARYLATES BASED ON CHALCONES

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ABSTRACT

Synthesis and characterization of UV-sensitive polyarylates based on chalcones have been described. Melting point, ^1H NMR spectrums, ^{13}C NMR spectrums, UV/VIS spectrums and IR. spectrums for 4,4'-dihydroxychalcone (BDHC), and 3-ethoxy-4,4'-dihydroxychalcone (BDHEC) have been confirmed during this study. Methods of preparation and study of UV-sensitive polyarylates have been described too. Tests for photoresists have been included in particular application.

INTRODUCTION

The synthesis of 4,4' - dihydroxychalcone (BDHC), and 3-ethoxy-4,4'-dihydroxychalcone (BDHEC) are here described. During this study a number of chemical and physical properties (including structure, UV absorption, melting point, etc.) are confirmed. The structures of both chalcones were confirmed by ^1H NMR, ^{13}C NMR and IR methods. These two chalcones were then used to prepare UV-sensitive polyarylates, which were studied as photoresists. During these investigations the application and UV properties of these polyarylates were checked.

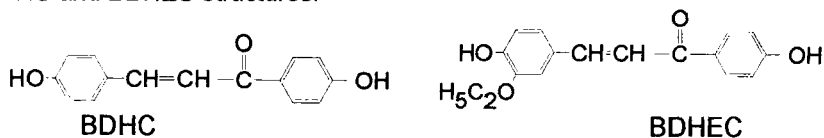
UV-sensitive polyarylates with UV active group in the main chain have been topics of study in our institute for several years [3 - 8]. This article only concerns polyarylates based on BDHC and on BDHEC. BDHEC in particular exhibits interesting properties, however both BDHC and BDHEC are highly UV-sensitive and easy to prepare and to purify. These properties are noteworthy because crosslinking with UV radiation is a very good method for preparation of microstructures on a silica surface, or for preparation of non-linear optical microstructures [9].

EXPERIMENTAL

Preparation of polyarylates.

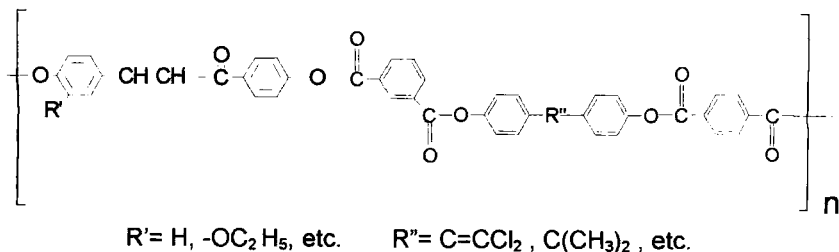
4,4' - dihydroxychalcone (BDHC) was prepared [1] by reacting a mixture of p-hydroxybenzaldehyde (0.8 mole) with p-hydroxyacetophenone (0.8 mole) dissolved in 1 dm³ absolute alcohol saturated with HCl gas, maintained at 5° C for 5h. The reddish violet crystals formed were filtered, washed thoroughly with distilled water, and dried in a vacuum oven at 100°C. The product was recrystallized in ethanol-water to obtain the pure product (violet crystalline powder) with a melting point of 208 °C (DSC method). 3-ethoxy-4,4'-dihydroxychalcone (BDHEC) was prepared by the same way, but by reacting a mixture of 3-ethoxy-4-hydroxybenzaldehyde with p-hydroxyacetophenone. The orange crystals formed were filtered and washed as above. The yellow pure product was a crystalline powder with a melting point of 231 °C (DSC method).

BDHC and BDHEC structures:



Polyarylates were prepared by the interfacial method. In a 1 L reactor equipped with a thermometer, added dropwise and mechanical stirrer the mixture of bisphenols was combined with NaOH aq (0.2 mol of bisphenols mixture with 0.2 mol NaOH in 150 cm³ of water). Into this solution 0.02 mol TEBA Cl (in 50 cm³ of water) was added as a catalyser of the interfacial reaction. Then 0.2 mol of a terephthaloyl chloride (2parts) and isophthaloyl chloride (1part) mixture in 300 cm³ of methylenedichloride was added slowly (30min at 20°C). Then 250 cm³ of methylenedichloride was added. After 30 min. of stirring excess NaOH was neutralized by addition of 5% HCl (aq.) After neutralization the organic layer was separated, washed by distilled water and added into 1 dm³ of acetone. During this process the polyarylate was set apart in the form of white - yellow flocks. These flocks were then dried in a vacuum oven at 100 °C. All polyarylates were prepared using the same method.

Polyarylates structure



METHODOLOGY:

The reaction products were identified by DSC analysis (melting point) using UNIPAN DSC 680 analyzer. The temperature rate was 5 °C per min. The samples were closed in air. Elemental analysis was performed using a Perkin-Elmer analyzers. IR spectroscopy was carried out with a Carl-Zeiss SPECORD M80 spectrophotometer. All analysis were done by the KBr tablet method. UV/VIS spectroscopy analyses for monomers were done in solution (the studied substances were dissolved in methanol. Sample concentrations for all measurements was $1.6 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$) at 298 K. UV/VIS experiments were done by the thin layer method; layers of the polymers were deposited on a quartz background and the thickness of each sample was measured prior to UV spectroscopy using an electronic thickness analyzer. UV measurements were done for samples which were irradiated for 0 sec., 30 sec., and from 60 sec. to 15 min. with a rate of 60 sec/ spectrum. Measurements of tenacity were done for samples in film form (Times of irradiation were as for measurements of UV absorption - see above). Sample width was constant at 10mm, as was length at 100mm. The thickness was measured for each sample before tenacity tests using mechanical apparatus. This apparatus provides a sample's stretching speed at 50 mm per min. All NMR analyses were done in CD_3OD solution, using a VARIAN VXR300 spectrometer. Contrast, resolution and UV sensitivity were checked by preparation of semiconductor microstructure on silicone monocrystal. A silicone background was prepared in an industrial semiconductor manufacturing process as follows:

a.) preparation of Si surface for deposition of UV sensitive polymers (RCA process in FSI-SATURN arrangement: $\text{H}_2\text{O}_2 + \text{NH}_3$ 90°C; washing in deionized water, $\text{H}_2\text{O}_2 + \text{HCl}$ 90°C, washing in deionized water, $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ 130°C, washing in deionized water, HF 30 sec., washing in deionized water, drying in warm nitrogen) b.) deposition of the polymer layer onto the Si surface in a centrifuge ($\text{rpm} = 3000 \text{ min}^{-1}$ 20 sec., polymer concentration was 3% (w), solvent was a mixture of 2 parts of methylene dichloride with 1 part of ethylene tetrachloride) c.) drying (GCA drier with nitrogen atmosphere), d.) UV crosslinking (Karl Suss MJB-21 arrangement with an HBO-250 high pressure mercuric lamp. During these tests a CANON MIT test mask was used) ,e.) development in chloroform and drying in warm nitrogen, etc.) visual estimation of samples under an OLIMPUS BHM microscope (POLAROID camera included).

RESULTS AND DISCUSSION

The elementary analysis of BDHC showed: %C 74.95 (calcd. 74.99), %H 4.88 (calcd.5.03). The elementary analysis of BDHEC showed %C 71.81 (calcd.71.83), %H 5.91 (calcd. 5.63).

IR results and absorption assignments: 1644 cm^{-1} (s) $\nu_{\text{C=O}}$ of carbonyl group, 1604 cm^{-1} $\nu_{\text{C=C}}$ of olefine, 976 cm^{-1} (m) $\nu_{\text{C=C}}$ of trans

CHR=CHR' alkene. The IR spectrum of BDHEC showed 1640 cm^{-1} (s) $\nu_{\text{C=O}}$ of carbonyl group, 1440 cm^{-1} (m) $\delta_{\text{C-H}}$ of -C- group, 1380 cm^{-1} (l) δ_{sym} of CH_3 , 1342 cm^{-1} (l) $\delta_{\text{C-H}}$ of CH_2 group, 972 cm^{-1} (m) $\nu_{\text{C=C}}$ of trans CHR=CHR' alkene.

UV/VIS analysis for BDHC showed: $\lambda_{\text{max}1} = 349\text{ nm}$ ($\epsilon = 28750\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), $\lambda_{\text{max}2} = 200\text{ nm}$. ($\epsilon = 14375\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), and for BDHEC showed: $\lambda_{\text{max}1} = 360\text{ nm}$ ($\epsilon = 30000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), $\lambda_{\text{max}2} = 260\text{ nm}$ ($\epsilon = 21875\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), $\lambda_{\text{max}3} = 204\text{ nm}$ ($\epsilon = 18125\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

The BDHC ^1H NMR spectrum in CD_3OD showed a complex multiplet at $\delta = 6.7\text{--}7.1$ ppm due to the aromatic protons H-C(3), H-C(5), H-C(3') and H-C(5') and another at $\delta = 7.6\text{--}8.2$ ppm due to H-C(2), H-C(6), H-C(2') and H-C(6') aromatic protons. The vinyl protons signals appear at $\delta = 7.65\text{--}7.8$ ppm. (two singlets). The BDHEC ^1H NMR spectrum showed a multiplet at $\delta = 6.9\text{--}7.0$ ppm. due to the aromatic protons H-C(4'), H-C(6') and a multiplet at $\delta = 8.0\text{--}8.1$ ppm. due to the aromatic protons H-C(3'), H-C(5') a multiplet at $\delta = 7.24\text{--}7.29$ due to the H-C(3) proton and a doublet at $\delta = 7.44\text{--}7.48$ ppm. due to the H-C(2) proton. Signals of aliphatic protons (from etoxy group) showed a quartet at $\delta = 4.20\text{--}4.40$ ppm. due to protons from a CH_2 group and a triplet at about $\delta = 2.8$ ppm. from a methylene group. The vinyl protons signals appear at $\delta = 7.65\text{--}7.7$ ppm. (two singlets). The BDHC ^{13}C NMR showed eleven signals which were at $\delta = 115.8$ ppm C(2,6), $\delta = 115.69$ ppm. C(2',6'), $\delta = 118.79$ ppm. vinyl carbon (close to the carbonyl group), $\delta = 126.94$ ppm. C(3,5), $\delta = 130.81$ ppm. C(4'), $\delta = 130.93$ ppm. C(4), $\delta = 143.41$ ppm. C(3',5'), $\delta = 159.72$ ppm. vinyl carbon (nearer phenyl), $\delta = 164.71$ ppm. C(1), $\delta = 187.56$ ppm. C(1'), $\delta = 205.94$ carbon from a carbonyl group. The BDHEC ^{13}C NMR showed fourteen signals which were at $\delta = 14.86$ ppm. due to the carbon in a CH_2 group, $\delta = 65.25$ ppm. due to the carbon in a CH_3 group, $\delta = 112.82$ ppm. C(5), $\delta = 115.99$ ppm. C(2',6'), $\delta = 116.09$ C(2), $\delta = 119.92$ ppm. C(3), $\delta = 128.29$ ppm. C(3',5'), $\delta = 124.15$ ppm. vinyl carbon (close to the carbonyl group), $\delta = 131.65$ ppm. C(4'), $\delta = 131.66$ ppm. C(4), $\delta = 144.43$ ppm. vinyl carbon (near phenyl), $\delta = 147.91$ ppm. C(6), $\delta = 162.44$ ppm. C(1'), $\delta = 150.25$ ppm. C(1), $\delta = 189.04$ ppm. due to a carbon in a carbonyl group.

BDHC and BDHEC were used to prepare of UV-curable polyarylates. The molar proportion of BDHC (or BDHEC) or uncrosslinkable comonomers is shown in table 1.

UV SENSITIVE PROPERTIES:

All of the reaction products shown in table 1 were studied as materials for photoresists. The application properties of these polyarylates were checked as follows.

The dependence of UV absorption and tenacity were investigated as function of irradiation time. The results are presented below:

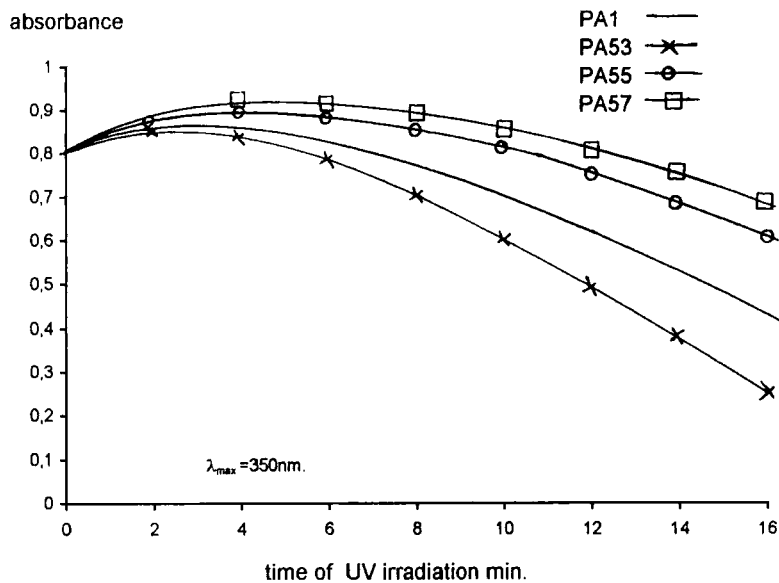


FIGURE 1 Dependence of UV absorption as a function of UV irradiation time.

TABLE 1 Molar proportion of BDHC, BDHEC and uncrosslinkable comonomers.

polyarylat	DIAN	CBP II	BDHEC	BDHC	reaction yield %
1.	2.	3.	4.	5.	6.
PA1	1	-	2	-	50.3
PA2	1	-	1	-	66.7
PA3	2	-	1	-	80.4
PA4	3	-	1	-	96.0
PA50	-	2	1	-	98.0
PA51	-	1	1	-	78.8
PA52	-	1	2	-	70.3
PA53	-	1	3	-	68.0
PA54	2	-	-	1	59.8
PA55	1	-	-	1	unknown
PA56	1	-	-	2	unknown
PA57	-	2	-	1	63.2
PA58	-	1	-	1	unknown
PA59	-	1	-	2	unknown

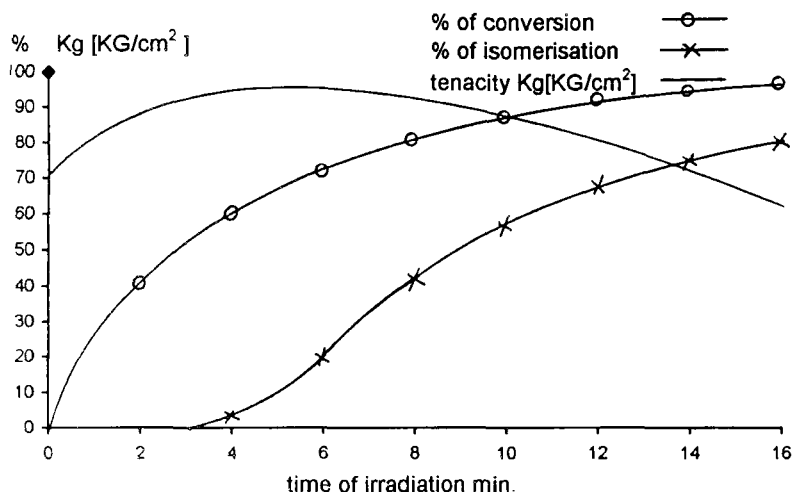


FIGURE 2 Dependence % of conversion (% of UV crosslinkable), % of isomerisation and tenacity as a function of UV irradiation time for polymer PA53.

After mechanical tests the content of $R-CH=CH-(CO)-R'$ groups were checked and the decrease in the number of this group during irradiation was observed. At the same time the amount of other isomers like $R-CH=CH-R'$ or $R-(CO)-CH=CH-(CO)-R'$ (note - these isomers were also observed during irradiation by Zahir [1]) was determined. According to these results it was possible to plot the dependence of the % of conversion (% of UV crosslinkable), % of isomerisation, and tenacity as a function of UV irradiation time. These curves for some polyarylates are shown in Figure 2.

Based on these studies the optimum irradiation time was found: 2 min. 30 sec. to 3 min. Application properties including: resolution, contrast, adhesion and resistance to acids were also checked. For the application studies only polyarylates PA1, PA2, PA52, and PA53 were examined. The other polyarylates did not meet basic requirements for photoresists (i.e. high UV sensitivity, high chemical resistance, high adhesion, high tenacity, good solubility in harmless solvents etc.). During the application tests these properties of the interesting polyarylates were determined. Due to the fact that some of the parameters (in particular: contrast and tenacity) were not satisfactory, 10 % active diluter in the form of methylmetacrylate was added into the solution of polyarylates in dissolver. This increased both contrast and tenacity.

TABLE 2: Application properties of polyarylates.

polymer	max. resolution μm and UV dose mJ/cm^2	max. contrast % without diluter/ with diluter	notices about polymer's surface
1.	2.	3.	4.
PA1	4/1200	80/14	good
PA2	4/1200	82/16	good
PA3	8/2000	88/18	quite good
PA4	8/2400	90/24	quite good
PA50	8/1200	79/14	quite good
PA51	8/800	76/11	good
PA52	4/1200	72/9	very good
PA53	4/800	71/8	excellent
PA54	8/2400	87/18	very poor
PA57	8/1200	88/24	very poor

CONCLUSION

Studies described in this report confirmed that polyarylates with BDHEC as a UV sensitive bisphenol show interesting properties.

- They dissolve well in THF and dioxane solvents, which are less harmful for the environment than the usually used dichloromethane or chloroform.
- The isomerisation of polyarylates with BDHEC during UV irradiation is slower than BDHC.
- Tenacity for polyarylates formed with BDHEC is higher than for polyarylates from BDHC (Polyarylates with BDHEC form a layer of polymers which is less crystalline).
- The solubility of polyarylates based on BDHEC (in particular BDHEC/ ChlorBisPhenol II compositions) is very good.
- Layers of polyarylates based on BDHEC have good adhesion to Si surface (better than polyarylates based on BDHC).
- Layers of polyarylates based on BDHEC do not have crystalline structures, a plus since such a layer has a higher tenacity.
- Polyarylates PA1 and PA53 with active diluter showed a very good resolution, contrast and UV sensitivity. These polyarylates also exhibit high tenacity and high chemical resistance even following irradiation.

We conclude that only polyarylates PA1 and PA53 with active diluter might potentially be used for photolithography processes, or in others

photopolymers applications. More information concerning these polyarylates, and photoepoxides based on BDHEC will be furthercoming.

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