

# P-27: Polyarylate Films for Optical Applications with Improved UV-Resistance

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## Abstract

Optical films can be made by novel polyarylates with improved UV stability, light transparency and heat-resistance. The present work relates to novel polyarylates made of bis(hydroxyphenyl)fluorene ortho disubstituted bisphenols. These materials feature a broad range of properties useful for optical applications, particularly for plastic and flexible FPD substrates.

## 1. Introduction

The results that will be shared in this paper deal with a study aiming at developing a polymeric film material to be used as a substrate for Liquid Crystal Displays and new emerging Display technologies. The most important features needed for materials used in Display applications are:

- ✓ Excellent Optical properties (transparency, very low birefringence)
- ✓ Excellent Thermal properties and Dimensional Stability to allow high temperature processing
- ✓ Good Mechanical properties to ensure strength and impact resistance and facilitate material handling
- ✓ Excellent Barrier properties to preserve functionality of the display.

All available materials, in fact, have limitations in one or more of these important characteristics.

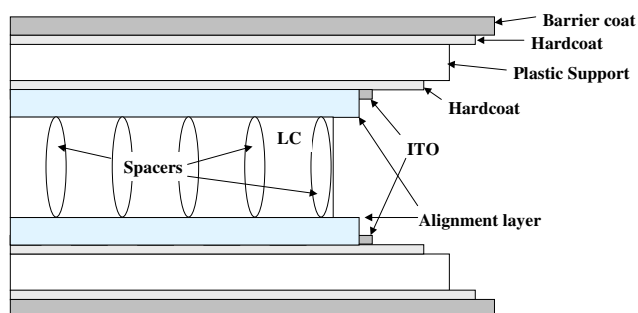
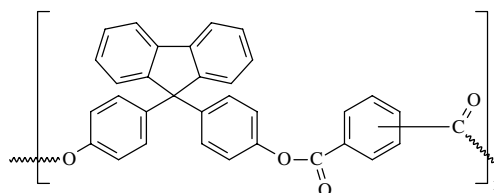


Figure 1 Schematic representation of a cross section of a plastic display

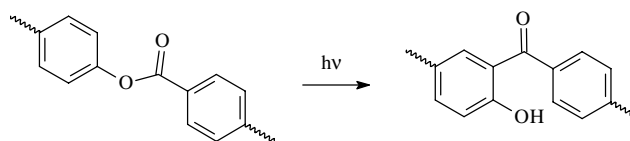
The fully aromatic Fluorene polyester, known in the art as FPE[1],



represents one of the most advanced product for this application. It shows very high thermal stability and mechanical, electrical and optical properties that make it very promising for use in electrical and optical applications. But the polyester chemical structure of FPE also presents a disadvantage concerning with two intrinsic limitations of this class of polymers: limited barrier effect ( $O_2$ ,  $H_2O$ , some chemicals) and an easily scratchable surface. FPE polyester, on the other hand, allows to deposit and bond to its surface functionalized coatings, showing very good adhesion properties: these, in turn, allow to achieve relatively high hardness values and provide a suitable base for inorganic coatings such as inorganic barriers and ITO layers.

A very important requirement for FPD applications is a higher light stability. Polyarylates with structure similar to FPE do not completely satisfy this requirement since they turn yellow when exposed to a light source (UV curing lamps, Xenon lamp or daylight) and their mechanical properties worsen.

Phenolic esters and polyesters are subject to a well known photochemical process called *the photo-Fries rearrangement* (1/C-hydro, 3/O-acyl-interchange)[2]:



As shown in the above scheme, this rearrangement proceeds to a cleavage of the ester bond followed by the transposition of the acyl group to the ortho position of the phenol. An o-hydroxybenzophenone structure is thus formed, which has an absorption in the range 320-450 nm giving the yellow coloration to the molecule. The process is prevalently an intramolecular

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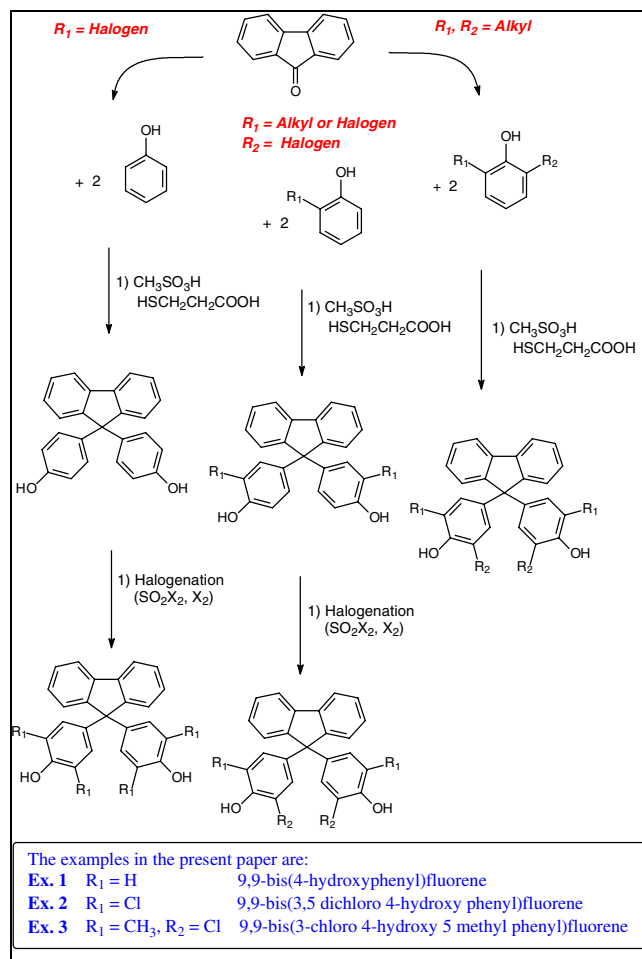
process and it cannot be stopped by the use of typical free-radical stabilizer like hindered phenols (BHT), or hindered amine-light-stabilizer (HALS).

A solution to this problem is to introduce a substituent in both the ortho-positions of the phenol groups[3]. These substitutions avoid the photo-Fries rearrangement, reducing drastically the yellowing of the polymer. At the same time, it is necessary that the polymer maintains the other important properties (thermal and mechanical) required for its applications.

We have found that only some substituent combinations[4] on the FPE structure give the best results in optical stabilization without a decrease of the thermal and mechanical properties of the polyarylate film. Experimental

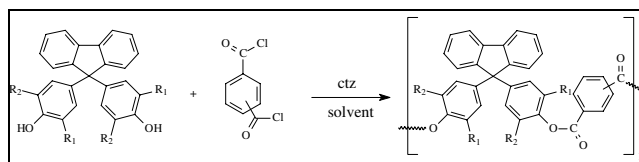
## 2.1 Synthesis

All the Fluorene bisphenols described in this paper are obtained according to the methods disclosed in literature[5] and shown in Figure 2.



**Figure 2 Synthetic scheme of o-disubstituted 9,9-bis bis(4-hydroxyphenyl)fluorene monomers**

All the polyarylates used in the examples are obtained by the polycondensation of the above-mentioned bisphenols with a 50% by mols mixture of terephthalic and isophthalic acid (Figure 3). The preparation methods used are reported in literature[6].



**Figure 3 Synthetic scheme of the o-disubstituted polyarylates**

## 2.2 Polymer Films

All the films are obtained by solvent casting using organic solvents, e.g. methylene chloride, N-methylpyrrolidone, etc. The 1-20% by weight dopes are cast on a smooth surface matching the requirements of thickness accuracy and surface smoothness needed by Display applications. The films are then dried in oven with a temperature ramp from 25° to 160°C then for 2hours at 160C.

## 2.3 Photo aging tests

All the polymer films (50  $\mu\text{m}$  thick.) described have been exposed to a light source reproducing the solar light spectrum (Xenotest, 1 hr exposure  $\equiv$  10 hrs. sunlight at noon) for 100 h. The exposed films are then evaluated with an UV-Visible spectrophotometer (Perkin-Elmer Lambda-9). Other UV sources can be used, with different spectra and total transferred energy. The exposure used in our tests is equivalent to  $18\text{mW}/\text{cm}^2$  in the whole lamp emission range, of which  $1.8\text{mW}/\text{cm}^2 = 6\text{J}/\text{cm}^2 \cdot \text{h}$  fall in the 320-400 nm (UV) range. The overall UV exposure is thus  $600\text{J}/\text{cm}^2$ .

## 2.4 Physical Measurements

Tensile stress-strain curves have been measured on polymer films (50  $\mu\text{m}$  thick, 50x15 mm rectangular samples) by an Instron 5564 dynamometer (ASTM D882) and the resulting mechanical characteristics are reported in Table 2. The same instrument, equipped with a thermostatic chamber, has been used to get a linear CTE (coefficient of thermal expansion) value in the 25°C – 75°C range. Thermal properties have been obtained on polymer powder by an Perkin Elmer DSC 4 and TGS-2.

## 3 Results

As shown in Table 1, samples Ex. 2, 3 show just a slight increase of absorbance in the range between 320 and 500 nm during the Xenon Lamp test. On the contrary, Ex. 1, (FPE, non-ortho disubstituted) increases dramatically its absorption by 15 times at 400 nm (blue absorption), resulting in a strong yellow coloration. Figure 3 and 4 show the UV-Vis spectra of the unexposed and 100 hours exposed films.

As shown in Table 2, Ex.2 and 3 show an improvement in mechanical properties versus Ex. 1. Ex. 2 and 3 show decomposition temperature values similar or slightly lower than the Ex. 1 and higher glass transition temperatures. This increase in Tg allows their use at higher process temperature during device assembling.

### 3 Conclusions

The results of our work indicate that these new polyarylates offer a set of material properties suitable for Display applications, specifically for plastic and flexible substrates needed for lightweight and robust portable devices. These polyarylates maintain all the properties that make the FPE polymer suitable for optical and electrical applications and add a higher resistance to UV-Visible light needed for processing and working life.

Film prototype samples are available at Ferrania Imaging Technologies for direct evaluation in Display assembling.

### Acknowledgments

Both the authors thank Mr. Roberto Bracco (*Ferrania Physical Evaluation Lab.*) for the physical measurements and Mr. Paolo Salvarani (*Ferrania Analytical Lab.*) for thermal evaluations of all the described samples.

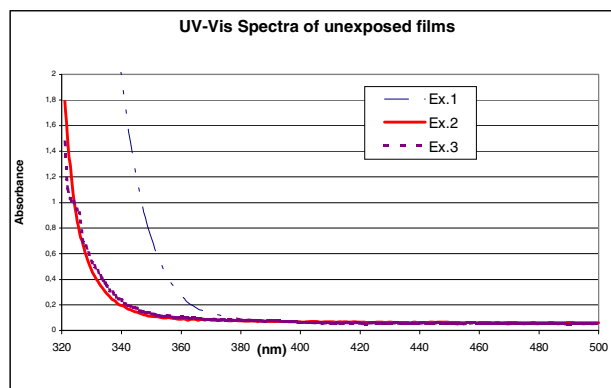


Figure 4 UV-Vis Spectra of unexposed films

Xenon Lamp Exposure Test (Absorbance units)						
$\lambda$ (nm)	0 hours			100 hours		
	Ex.1	Ex.2	Ex.3	Ex.1	Ex.2	Ex.3
321	5.0000	1,7906	1,4715	5.0000	3,3091	4,5502
330	4.4852	0,4671	0,5364	4.3668	1,2956	1,9243
340	1.9880	0,1951	0,2384	5.0000	0,8003	1,1731
350	0.7233	0,1126	0,1329	5.0000	0,5831	0,8399
360	0.2711	0,0876	0,1050	3.4697	0,4573	0,6341
370	0.1337	0,0804	0,0907	3.0427	0,3611	0,4891
380	0.0893	0,0757	0,0853	2.3214	0,2891	0,3797
390	0.0763	0,0708	0,0795	1.6069	0,2258	0,2832
<b>400</b>	<b>0.0721</b>	<b>0,0692</b>	0,0591	<b>1.0200</b>	<b>0,1820</b>	0,2177
500	0.0607	0,0597	0,0513	0.0710	0,0668	0,0634

Table 1 UV-Visible absorption data on unexposed and Xenon-lamp aged (100 hrs) films

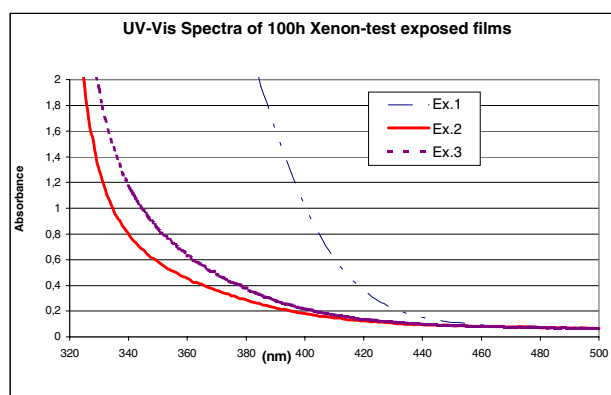


Figure 5 UV-Vis Spectra of 100 hours Xenon-test exposed films

	Ex.1	Ex.2	Ex.3	PET*	PES*	PC*	Kapton 200HN*
Ultimate tensile strength (MPa)	100	120	100	55	83-100	52-72	221
Young modulus (GPa)	2.9	3.4	2.8	2.5-3.0	2.4-8.6	2.1-2.4	2.8
T <sub>g</sub> (DSC) (°C)	330	342	346	76.5	228	150	385
T <sub>dec</sub> O <sub>2</sub> (TGA) (°C)	415	385	387	-	-	-	-
T <sub>dec</sub> N <sub>2</sub> (TGA) (°C)	413	394	392	-	-	-	-
Birefringence	7.9exp-5	comparable	comparable	-	-	-	-

\* Data from <http://www.matweb.com>

Table 2 Mechanical and thermal properties of the unexposed films

- [1] P.W. Morgan, *Macromolecules*, **3**(5), 536-544 (1970)  
 [2] J. March, "Advanced Organic Chemistry", 4<sup>th</sup> edition, John Wiley and Sons, New York, 1992, 556; H. Kobsa, *J. Org. Chem.*, **27** (7), 2293-2298 (1962); D. Bellus et al., *Chem. Rev.*, **67** (6), 599-609 (1967); D. Bellus et al., *J. Polym. Science: Part C*, **16**, 267-277 (1967); S. B. Maerov, *J. Polym. Science Part A*, **3**, 487-499 (1965)  
 [3] J. Lo, S.N. Lee, E.M. Pearce, *J. Appl. Polym. Sci.*, **29**, 35-43 (1984)

- [4] Italian Patent Application No. SV2000A000053, filed on Nov. 14, 2000  
 [5] US 5,248,838, *Massirio et al.*, Ex.5.  
 [6] EP 0396418(B1), *Hampl et al.*, Ex.1.