

Thin-Film Polyimide/Indium Tin Oxide Composites for Photovoltaic Applications

Angel E. Lozano,¹ Javier de Abajo,¹ José G. de la Campa,¹ Cecilia Guillén,² José Herrero,² María Teresa Gutiérrez²

¹Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006 Madrid, Spain

²Departamento de Energías Renovables, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Avenida Complutense 22, 28040 Madrid, Spain

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ABSTRACT: Soluble polyimides were prepared from suitable monomers and were evaluated for their thermal and mechanical properties. The polymers were processed into films for use as supports for transparent, conductive indium tin oxide (ITO) layers. After deposition, annealing *in vacuo* at temperatures up to 400°C was performed to test the ability of the materials to endure typical device fabrication temperatures without damage to the ITO-coated polymeric substrate. The evolution of the structural, optical, and electrical characteristics with the annealing temperature was analyzed and compared with that of polymeric and conventional glass substrates as references. Polyimide 6F6F, syn-

thesized from hexafluoroisopropylidene diphthalic dianhydride and hexafluoroisopropylidene dianiline, had optimal characteristics for photovoltaic applications, permitting the achievement of conductive, ITO-coated samples with optical transmission greater than 75% in the visible and near-infrared wavelength ranges, without significant deterioration of their properties after vacuum annealing at temperatures up to 350°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3491–3497, 2007

Key words: coatings; composites; polyimides; surfaces; thin films

INTRODUCTION

Indium tin oxide (ITO) layers are commonly used as frontal electrical contacts in various thin-film photovoltaic technologies.¹ Such photovoltaic devices have been generally developed on glass substrates, but the replacement of glass by polymer foils is attracting increasing interest to reduce manufacturing cost and to achieve flexible and lightweight power sources. The key requirements of ITO-coated polyimide films for photovoltaic applications are high optical transmittance in the visible range and high electrical conductivity. Concerning ITO layer preparation by the sputtering method, substrate heating or postdeposition annealing at temperatures above 250°C is reported to be needed to improve the film properties, mainly the conductivity.^{2,3} However, when polymeric

substrates are used, the annealing temperature is generally limited by the thermal resistance of the polymer.

Polyimides are an important family of organic materials that have an excellent balance of thermal and mechanical properties. They were marketed in the 1970s as films and enamels for high-temperature electrical insulators, and since then they have found many applications as high-performance polymers in advanced technologies.^{4,5} Because of their aromatic nature and the strong interchain attraction forces and because of the special synthesis route, which involves a heating treatment at 300°C or higher,⁶ conventional polyimides are colored materials that do not fit the requirements of transparency and light transmittance needed for optical applications. However, since the commercialization of the first polyimides, a great number of polyimides have been described, covering a very wide range of properties. Thus, advances have been achieved that have led to polyimides with better processability and improved specific properties, such as photosensitivity, lack of color, light transmission, adhesion, dimensional stability, electrical conductivity, and good planarization.^{7,8}

In previous studies of the capabilities of polyimides as structural substrates for thin-film photovoltaic devices, the deposition of transparent and conductive ITO layers onto Kapton, a traditional polyimide made from oxydianiline and pyromellitic dianhydride, has

Correspondence to: J. de Abajo (deabajo@ictp.csic.es).

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been reported.^{9,10} Even though Kapton was the first polyimide to be marketed, its properties still appear to be unique in terms of the price/performance ratio. Nevertheless, new technologies are demanding materials with improved properties, and chemical modifications of traditional polyimides have allowed the development of novel materials that are being evaluated for applications for which specific properties are needed. Some of the most promising materials in this respect are fluorine-containing polyimides, which have been extensively studied because they offer particularly good solubility, high thermal resistance, and absence of color.^{4,11,12}

The aim of this work has been to prepare noncommercial polyimides and to evaluate their performance for this specific application in comparison with traditional materials. Because a lack of color and light transmittance are mandatory characteristics for any material to be considered as a candidate, monomers should be chosen that can lead to amorphous, colorless polymers. Therefore, in this work, monomers have been used that bear the structural elements to impart these properties to the final polymers.

The work has been outlined as an integral project, starting from selected monomers and then synthesizing polyimides, which could be processed into films to be used as supports of transparent, conductive ITO layers. These ITO layers have been deposited by radio frequency (rf) sputtering at room temperature onto the surface of the polyimides and also onto conventional soda-lime glass substrates as references. The composite materials fabricated in this way have been thoroughly characterized and evaluated for photovoltaic applications, and a comparative study has been performed to establish the relationship between the polymer chemical structure and photoelectronic behavior.

EXPERIMENTAL

Materials

Hexafluoroisopropylidene diphthalic anhydride (Chriskev, Kowloon, Hong Kong) and biphenylene tetracarboxylic acid dianhydride (Ube, Tokyo, Japan) were purchased in a monomer grade, and they were purified by sublimation just before use. Isophthaloyl diphthalic anhydride was prepared and purified as previously reported.¹³ Hexafluoroisopropylidene dianiline (Chriskev) and oxydianiline (Aldrich, Milwaukee, WI) were purified by recrystallization from suitable solvents and were purified by sublimation just before use.

Polymers and films

Polyimides were prepared by the polycondensation of equimolar amounts of dianhydride and diamine in a solution of *N,N*-dimethylacetamide (DMA) at a low

temperature to yield the corresponding poly(amic acid) intermediate. To the viscous solution of the intermediate, a mixture of acetic anhydride and pyridine was added, and the imidation reaction was allowed to proceed for 24 h at 50°C. The polymers were isolated by precipitation in an excess of water and ethanol and then purified by thorough washing with ethanol and subsequent extraction in a Soxhlet apparatus with ethanol for 20 h. The yields of the polymers were virtually quantitative.

Polymer films were prepared by the casting of filtered polymer solutions in DMA (8% w/v) on a leveled glass plate placed in a vacuum oven. The solvent was evaporated by heating at 80°C for 8 h at atmospheric pressure and finally *in vacuo* at 120°C for 24 h. The glass plate was then removed from the oven and dipped in warm water to lift the film, which was extracted with methanol for 24 h in a Soxhlet apparatus and finally dried at 90°C for 12 h in a vacuum oven.

ITO thin films were deposited onto the polyimides and conventional glass substrates by an rf-sputtering process that has been reported in previous works.^{9,10} The sputtering target was In₂SnO₃ with a composition of 95:5 (wt %). Before the deposition, a pretreatment of the substrate surface was performed by the adjustment of the nitrogen flow and plasma power.¹⁰ In this way, the adherence of the sputtered layers to the polymeric foils was improved. Thin deposition was carried out at room temperature without substrate heating, and after deposition, the ITO-coated samples were annealed *in vacuo* at 300, 350, or 400°C for 30 min. Films attained by this methods showed good mechanical properties and could not be fractured in a proper manner unless the samples were dipped into liquid nitrogen for breaking.

Measurements

Infrared spectra of polymer films were recorded on a Nicolet 750 Magna-IR spectrometer (Waltham, MA). An attenuated total reflection device (model 300 with a Ge crystal, Spectra Tech) was used in all cases. Glass-transition temperatures for the various polyimides were determined with a PerkinElmer DSC-7 (Wellesley, MA) at a heating rate of 20°C/min under N₂ from 50 to 400°C. The samples were scanned twice, and the midpoint of the endothermal displacement of the second run was taken as the glass-transition temperature. Thermogravimetric analyses were performed with a PerkinElmer TGA-7 thermobalance at 10°C/min under N₂. The inherent viscosities were determined in an automated Ubbelohde viscometer with 0.5% (w/v) DMA solutions at 25 ± 0.1°C. The tensile strength of the films was measured on an Instron 1122 dynamometer (Norwood, MA) at 25°C with an extension rate of 2 mm/min and a gauge length of 10 mm.

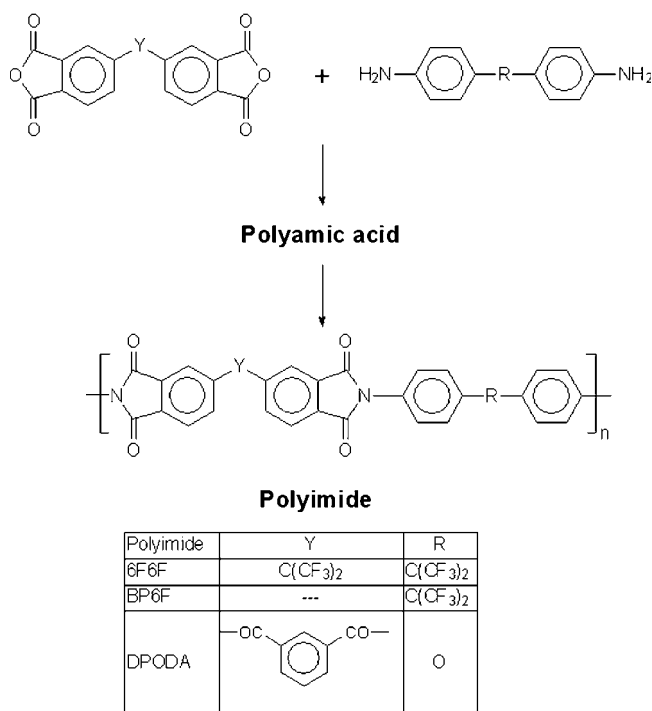


Figure 1 Polycondensation route for the preparation of the polyimides.

Environmental Scanning Electron Microscopy (ESEM) micrographs were taken with a Philips XL30 ESEM device operating at 15 kV. The samples were previously coated with a thin layer (2–3 nm) of gold and palladium by a Polaron SC7640 sputtering coater operating in an argon atmosphere at 3×10^{-3} mbar.

The crystalline structure of the ITO layer was analyzed by X-ray diffraction (XRD), with a nickel-filtered Cu K α 1 emission line ($\lambda = 1.5405 \text{ \AA}$), in a Philips X'pert instrument.

Optical measurements of the bare and ITO-coated substrates were made with unpolarized light at normal incidence in the wavelength range of 250–1500 nm with a PerkinElmer Lambda 9 double-beam spectrophotometer. The electrical sheet resistance of the coatings was determined with the four-point-probe method with a Veeco model FPP5000 system directly pressing down the sample on the four-point probe without making metal electrical contacts on the samples. Taking into account the thickness of the ITO layers, which was measured with a Dektak 3030 sur-

face profile system (Sloan Technology Corp., Santa Barbara, CA), and the electrical sheet resistance, we determined the electrical resistivity of the samples.

RESULTS AND DISCUSSION

The preparation of the experimental polyimides was carried out by conventional means with diamines and dianhydrides with a variety of chemical structures. The polycondensation route is depicted in Figure 1.

Polyimide 6F6F was previously reported and in fact was even marketed in semicommercial amounts in the 1990s under the name Sixsef-44 (American Hoechst) for electronics, and the polymer has been investigated for its ability as a barrier material for gas separation.^{14,15}

Fourier transform infrared spectroscopy was used to identify the polymers, and their molecular weights were estimated with viscometry. An inherent viscosity of about 1.0 dL/g indicated weight-average molecular weights greater than 5×10^4 g/mol.¹²

The polymers also were characterized by their thermal transitions and their thermal resistance, which are summarized in Table I.

The glass-transition temperatures, measured by differential scanning calorimetry, were in the range of 250–330°C, confirming that the presence of flexible linkages in the main chain, as ether or carbonyl, helped in lowering the glass-transition temperature. No evidence of crystallinity was observed by differential scanning calorimetry (Quorum Technologies, New Haven, UK) because no melting endotherm was detected in the range of 50–400°C for any of the polymers. The decomposition temperatures, taken as the temperatures of the initial weight loss by thermogravimetric analysis, were over 500°C for all the polymers, and this in agreement with the excellent thermal resistance of aromatic polyimides in general. Evidently, the chemical modifications performed in this work did not greatly impair the thermal stability with respect to traditional polyimides.

The polymers of this report were soluble in organic polar solvents, such as DMA and *N*-methylpyrrolidone, and polymer 6F6F was soluble even in chloroform, so films of all the polymers could readily be fabricated via casting and the controlled elimination of the solvent. The films were nearly colorless to slightly

TABLE I
Polyimide Properties

Key	Inherent viscosity (dL/g)	Glass-transition temperature (°C)	Decomposition temperature (°C)	Tensile strength (MPa)
6F6F	0.92	330 ^a	500	82
BP6F	1.02	315	520	103
DPODA	0.88	254	560	112

^a 320°C in ref. 10.

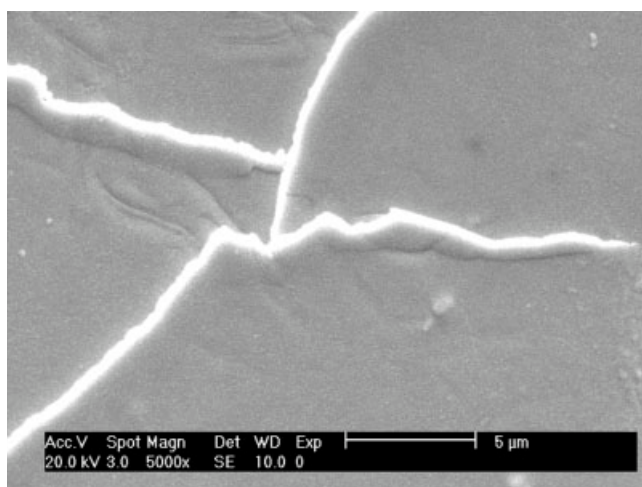


Figure 2 Scanning electron microscopy image of ITO on the polyimide DPODA.

yellow and showed good mechanical resistance. The thickness of the films tested in this work was about 50 μm , but the good solubility and excellent mechanical properties (tensile strength > 80 MPa) of the current polyimides should allow for a wide range of thicknesses if needed.

Figure 2 shows a micrograph of the film surface after ITO deposition. The crystal growth was greatly promoted around surface microdefects and scratches, which could be observed on uncoated films; a continuous, smooth ITO layer homogeneously covered the rest of the polymer surface. Uncoated areas were not observed, and a continuous layer of conductive, inorganic material was the result of ITO deposition on the polyimide substrates.

As for the compactness of the composite dense membranes prepared as described previously, two characteristics are to be noted: (1) the polymer matrix was dense, compact, and apparently free of micro-

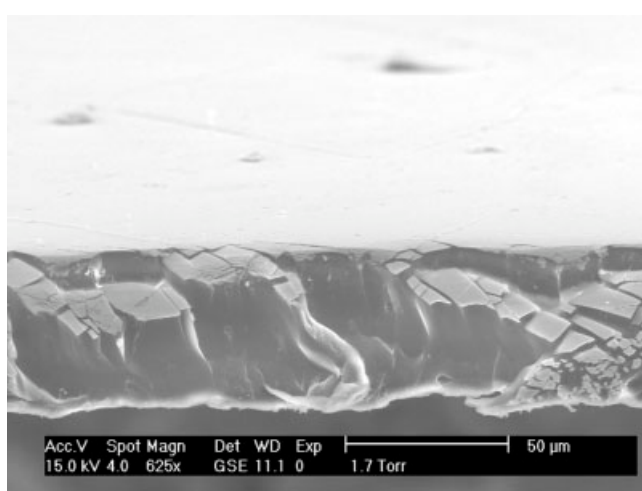


Figure 3 Scanning electron microscopy image of the ITO-coated DPODA polyimide sample.

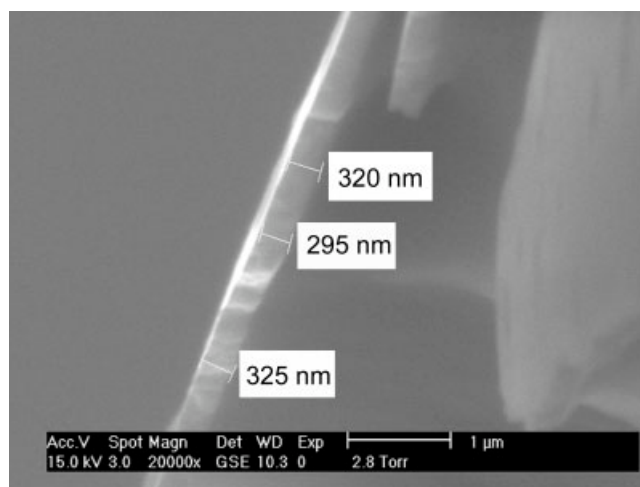


Figure 4 Scanning electron microscopy image of the ITO layer (ca. 300 nm thick) on the polyimide film.

voids, and (2) the adhesion of the ITO layer to the organic film was reasonably acceptable because the linear expansion coefficient of aromatic polyimides is $2\text{--}5 \times 10^{-5} \text{ K}^{-1}$, that of soda-lime glass is $6 \times 10^{-6} \text{ K}^{-1}$, and that of ITO is $8 \times 10^{-6} \text{ K}^{-1}$. Additionally, fracture micrographs of the composite materials (Fig. 3) clearly indicated that each component broke in a different fashion, with the polymer showing the usual clean fracture of tough, glassy polymers and the ITO layer breaking into small pieces, as was actually to be expected for a brittle, highly crystalline, inorganic material. The detailed cross-section micrograph of one of the composites is shown in Figure 4, in which the layer of ITO appears as a continuous coating of approximately 300 nm.

The crystalline structures of the ITO coatings on the various polyimides and on conventional glass sub-

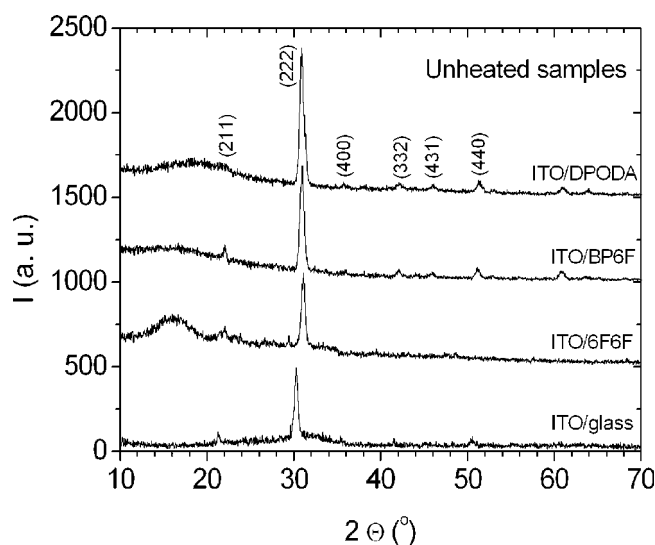


Figure 5 XRD data for the unheated, ITO-coated polyimides and glass substrates.

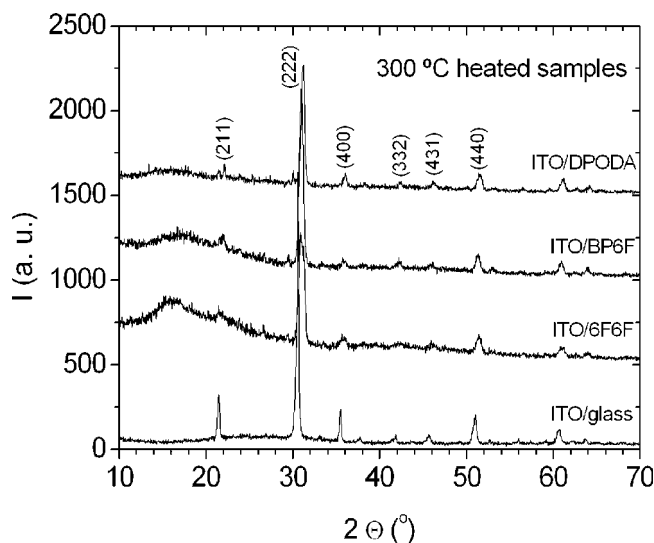


Figure 6 XRD data for the ITO-coated samples after annealing at 300°C in a vacuum atmosphere.

strates were determined by XRD measurements. Figures 5 and 6 show the behavior of the samples before and after heating at 300°C *in vacuo*, respectively. The assigned peaks were related to the crystalline ITO with a body-centered-cubic structure.¹⁶ A quality index that gives prominence to the preferential orientation of the crystallographic planes for this structure is the intensities ratio of crystallographic planes (222) and (400): $I(222)/I(400)$ ratio, which equals 3.33 for a random orientation of the crystallites. Figure 5 shows that for the ITO films grown onto the different substrates, the value of this ratio is higher than a random value, indicating a preferential orientation of the crystallites toward the (222) crystallographic plane. Such preferential orientation remained after heating at 300°C *in vacuo*. An important crystallinity enhancement was observed for the annealed ITO layer on the glass substrate (Fig. 6), as indicated by the increase in the intensity and the decrease in the full width at half-maximum of the main diffraction peaks. The additional crystallinity improvement that was gained on annealing was less significant for the ITO films on the polyimide foils, probably because during the heating and subsequent cooling, the ITO films underwent a higher mechanical stress on polyimide films than on glass substrates.

The optical transmittance spectrum of the samples was measured in the wavelength range of 250–1500 nm. Because the reference used during the measurements was air, the transmittance of the bare substrates was also measured for comparison and is depicted in Figure 7 for glass and the various polyimides.

The optical transmittance of the ITO-coated samples is presented in Figure 8.

To perform a more detailed analysis of the optical characteristics, the average transmittance values of

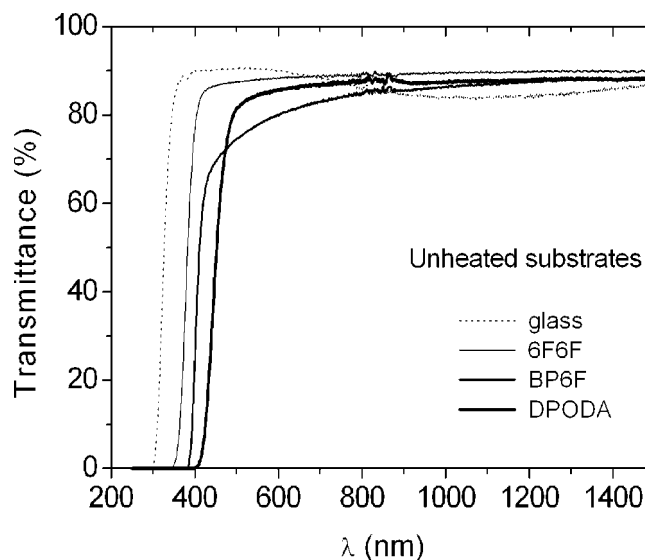


Figure 7 Optical transmission spectra for the bare polyimides and glass substrates.

the ITO-coated samples in the visible (400–800 nm) and infrared (800–1500 nm) ranges were calculated from the corresponding spectra, and the results are shown in Figures 9 and 10 as functions of the annealing temperature.

The 6F6F polyimide allowed average transmittances greater than 75% to be obtained in both the visible and infrared wavelength ranges, close to the values obtained for the conventional glass substrate and higher than that reported for Kapton.¹⁰

The substitution of 6F6F for Kapton brought about an increase in the optical transmittance below 400 nm that could increase the solar irradiance to the photoactive material by more than 7 W/m². On the other hand, the average visible transmittance decreased to

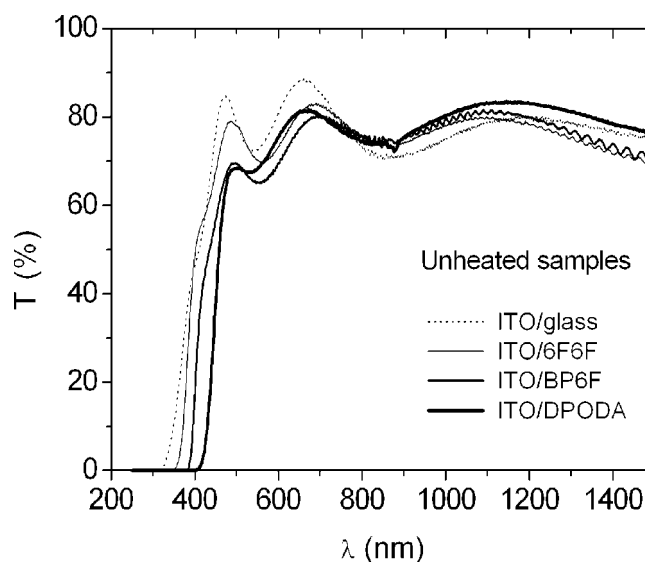


Figure 8 Optical transmission spectra for the ITO-coated samples (T = transmittance).

70 and 65% for the unheated BP6F and DPODA polyimides, respectively. After annealing *in vacuo* at temperatures up to 350°C, the drop in the average transmittance was only about 5% for the ITO-coated 6F6F samples but higher than 15% for the other polyimides. This result is in agreement with previous measurements of polyimides in optical applications. As a matter of fact, light guides from polyimides containing the bridge hexafluoroisopropylidene have shown substantially higher retention of light transmittance than polyimides containing oxydiphenylene or carbonyl linkages.^{4,7} Thus, these results confirm the superior properties of fluoro-containing polyimides for these applications.

All the tested ITO-coated organic substrates deteriorated when the temperature was raised to 400°C. Thus, regardless of the nature of the linkages joining *p*-phenylene moieties in the main chain, the chemical structure of the polyimides did not withstand heating above 400°C, and they lost their optical properties quite rapidly if so heated. The most stable materials seemed to be those containing ether linkages, which retained 60% of their transmittance in the infrared region, whereas those containing C(CF₃)₂ linkages retained only 35% of their infrared transmittance. This premature degradation of the C(CF₃)₂ composites did not occur with neat polyimides, and this may indicate that a special interaction took place between the substrate and the ITO layer, depending on the actual chemical composition of the organic material.

Before their degradation, ITO-coated polyimides and glass substrates showed almost the same infrared transmittance values, which decreased as the anneal-

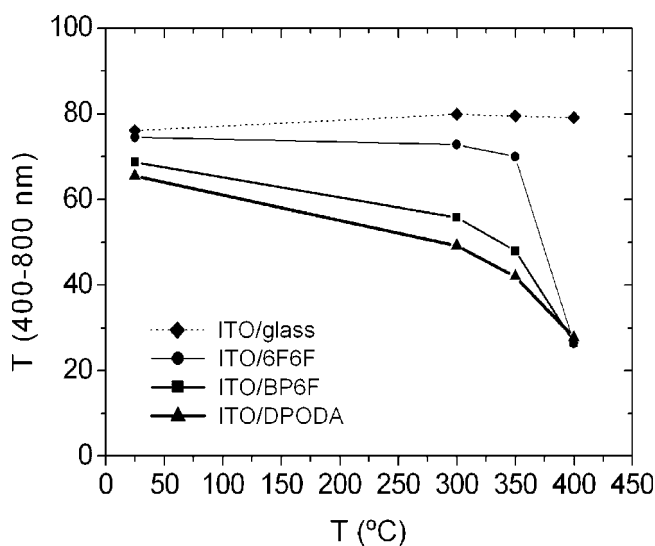


Figure 9 Average transmission values in the visible spectral range (400–800 nm) for the different ITO-coated samples as a function of the vacuum annealing temperature (T on the x axis = temperature; T on the y axis = transmittance).

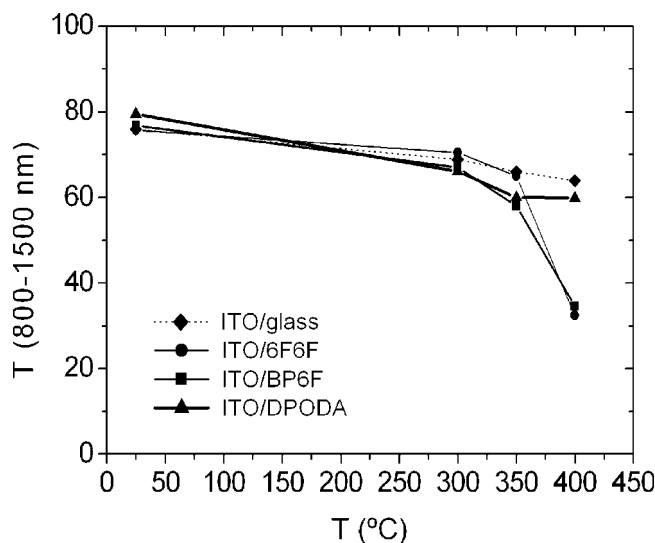


Figure 10 Average transmission values in the infrared spectral range (800–1500 nm) for the ITO-coated samples as a function of the vacuum annealing temperature (T on the x axis = temperature; T on the y axis = transmittance).

ing temperature increased. The decay in the infrared transmittance of the ITO layers when the vacuum annealing temperature was increased could be related to the increase in the carrier concentration as the oxygen vacancies in the material rose.¹⁷ This was in accordance with the electrical resistivity, which showed a drop from 1.5 mΩ cm for the untreated ITO–polyimide and ITO–glass composites to 0.8 mΩ cm after annealing at 350°C *in vacuo*. In general, the electrical conductivity of the ITO thin films with a fixed Sn dopant concentration is determined by the oxygen vacancies and the grain size, which are responsible for the carrier density and mobility, respectively. In other reports,^{3,18} a decrease in the sheet resistance with an increasing annealing temperature was attributed to the grain growth or crystallinity of ITO films. In these samples, such crystallinity enhancement was detected only for the annealed ITO layers on glass substrates, so it is thought that the conductivity increase was mainly due to the increment in the carrier concentration, especially for the ITO layers deposited onto the polyimides.

CONCLUSIONS

Three aromatic polyimides containing $-\text{CO}-$, $-\text{O}-$, and $-\text{C}(\text{CF}_3)_2-$ linkages were prepared by conventional means and characterized by their spectroscopic and thermal properties. Because of their special chemical composition, the polymers were amorphous and soluble, and this allowed the fabrication of transparent films of good mechanical properties by the casting of polymer solutions. Transparent and

conductive ITO coatings about 300 nm thick were deposited by radio frequency sputtering magnetron sputtering at room temperature onto the three aromatic polyimide films and a conventional glass substrate employed as a reference. The evolution of the structural, optical, and electrical characteristics of the ITO-coated polyimides arising from the postdeposition annealing temperature was analyzed.

The experimental results reported here demonstrate that the crystallinity improvement gained on annealing is less significant for ITO films on polyimide substrates than on glass substrates. Therefore, it is thought that the decrease in the electrical resistivity to 0.8 m Ω cm for ITO films on polyimide substrates after annealing was mainly due to the increment in the carrier concentration. Polyimide 6F6F has optimal characteristics for photovoltaic applications, permitting the achievement of conductive, ITO-coated samples with optical transmission greater than 75% in the visible and near-infrared wavelength ranges, without significant deterioration of the properties after vacuum annealing at temperatures up to 350°C. These transmission values are close to those obtained for a conventional glass substrate and higher than that reported for Kapton. In this respect, the use of 6F6F as a substitute for Kapton as a substrate involves an increase in the optical transmittance below the 400-nm wavelength that could roughly mean increasing the solar irradiance to the photoactive material by more than 7 W/m².

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