

Synthesis, Characterization, and Xerographic Electrical Characteristics of Perylene-Containing Polyimides

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ABSTRACT: A series of perylene-containing polyimides and copolyimides have been synthesized and characterized by DSC, TGA, NMR, UV–vis, and X-ray powder diffraction measurements. Xerographic electrical measurements indicated that perfectly alternating copolyimides had higher photosensitivities than those of homopolyimides and random copolyimide. After annealing, polyimide films showed a red-shift in UV–vis absorption and improved photosensitivity due to an increase in crystallinity, as indicated by wide-angle X-ray diffraction measurements.

Introduction

Most electrophotographic devices are composed of an organic-based multilayered system.¹ A typical device consists of a conductive metalized plastic base coated with a thin layer of photoconductive pigment dispersed in a polymer binder and overcoated with a transparent and mechanically tough charge transport layer consisting of a polymer doped with a molecule that conducts only one type of electrical charge (holes or electrons). In this system, stable photogenerator pigment dispersion is crucial since pigment setting or aggregation affects its photoconductive properties. Numerous organic pigments exhibiting high light absorbance in the visible region of the spectrum are known, and some of these, such as perylene, squaraine and azo pigments, have been successfully used.² To be effective, such pigments must also be capable of crystallizing in acceptable solid forms (polymorphism). Among various classes of pigments, the perylene bisimides are remarkable in the diversity of colors that can be obtained in the solid by simply modifying the groups attached on the periphery of the perylene chromophore. The phenomenon known as crystallochromy³ has been investigated by Graser and Hadicke and their collaborators,⁴ who determined the crystal structure of a variety of perylene bisimides and were able to relate the color to the degree of π -interactions, or molecular overlap, in the solid. A theoretical study on the crystallochromy of perylene bisimides has also been done by Kazmaier and Hoffmann.⁵

It would be ideal to develop a polymeric material that functions as a binder as well as a photogenerator, which would circumvent problems related to dispersion stability but would not unfavorably alter the xerographic properties. As a binder, the polymer should be of high molecular weight and melt or solution processable. To be used as a photoreceptor, it should be soluble in organic solvent for thin-film coating and display a high level of charge acceptance, good insulation in the dark,

and high conductivity in the light. However, most known polymers containing the perylene or perylene-tetracarboxylic bisimide moiety in the side chain and main chain were of low molecular weight and exhibited poor solubility in organic solvents.⁶ Only a few soluble high molecular weight polyimides containing a perylene-bis(carboximido) unit⁷ and a substituted perylenetetracarboxylic bisimide unit⁸ have been reported. In this paper, the synthesis, characterization, and xerographic electrical characteristics of various polyimides having perylenetetracarboxylic bisimide in the main chain are described.

Experimental Section

Materials. Aliphatic diamines **2a–f**, *m*-cresol, and isoquinoline were purchased from Aldrich Chemical Co. and used as received. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, **5d**) was polymer grade and purchased from ChrisKev Co. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, **5c**) was polymer grade and obtained as gift from Allco Co. 1,1,2,2-Tetrachloroethane (TCE), dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), deuterated trifluoroacetic acid, and other common organic solvents (Aldrich) were reagent grade unless otherwise stated and used as received. 3,4,9,10-Perylenetetracarboxylic acid dianhydride (**1**), purchased from Aldrich, was converted to the tetrapotassium salt of the tetracarboxylic acid using aqueous potassium hydroxide solution. After filtration, the filtrate was acidified with aqueous hydrochloric acid solution (ca. 2 M) to yield a mixture of dianhydride **1** and its tetracarboxylic acid, which was collected by filtration and dried in a vacuum oven at 150 °C. Binaphthalic dianhydride **5a**⁹ and diphenylprehnitic dianhydride **5b**¹⁰ were prepared according to literature procedures.

Monomer Synthesis. Diamine 4. 1,12-Diaminododecane (**2f**) (76.6 g, 0.38 mol) was dissolved in 80 mL of *m*-cresol with 0.5 g of isoquinoline, and the solution was heated to 200 °C. To this mixture was added a slurry solution of dianhydride **1** (10.0 g, 25.48 mmol) in *m*-cresol (40 mL) over 40 min. The reaction mixture was stirred at 200 °C for 5 h, cooled to room temperature, and poured into 300 mL of methanol. The precipitated solid was then filtered off, washed with methanol, and dried in air to yield 16.5 g (86%) of crude product. The crude product was extracted with hot *o*-dichlorobenzene to give

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pure diamine **4**: 9.3 g (48%); mp >300 °C; IR (KBr, C=O) 1691, 1653 cm⁻¹; ¹H NMR (300 MHz, CDCl₃/CF₃CO₂D) 8.80 (4H, q), 6.79 (2H, s), 4.29 (2H, t), 3.18 (2H, t), 1.79 (4H, m), 1.31 (16H, m); ¹³C NMR (75 MHz, CDCl₃/CF₃CO₂D) 165.67, 135.96, 133.29, 129.51, 126.57, 124.50, 122.56, 42.13, 41.78, 41.67, 29.56, 29.47, 29.35, 29.30, 28.92, 28.07, 27.38, 27.14, 26.09. Anal. Calcd for C₄₈H₆₀N₄O₄: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.04; H, 8.12; N, 7.28.

Polymer Synthesis. Care must be taken during the synthesis and purification of these polyimides since the xerographic property depends on the purity of the final products. All polymers must be washed thoroughly to remove any oligomers and dried free of solvents.

Typical Procedure for the Syntheses of Polyimides 3a–f. In a three-necked, round-bottomed flask equipped with a nitrogen inlet and outlet were added dianhydride **1** (0.517 g, 1.318 mmol), diamine **2f** (0.264 g, 1.318 mmol), *m*-cresol (20 mL), and isoquinoline (1 mL). The mixture was heated to 180–200 °C under nitrogen for 6 h and then cooled to room temperature. The resulting dark red solution was poured into acetone (300 mL). The resulting solid was washed repeatedly with aqueous sodium hydroxide (1 N) solution, followed by water and acetone. After drying under vacuum at 150 °C overnight, polyimide **3f** was obtained as a dark red solid (0.65 g, 88%). Completion of imidization was confirmed by infrared spectroscopy.

3a: 84%. Anal. Calcd for C₂₉H₁₈N₂O₄: C, 75.8; H, 4.2; N, 6.1. Found: C, 75.4; H, 4.11; N, 5.88.

3b: 86%. Anal. Calcd for C₃₁H₂₂N₂O₄: C, 76.4; H, 4.8; N, 5.7. Found: C, 76.4; H, 4.76; N, 5.91.

3c: 86%. Anal. Calcd for C₃₂H₂₄N₂O₄: C, 76.6; H, 5.0; N, 5.6. Found: C, 76.2; H, 4.96; N, 5.74.

3d: 88%. Anal. Calcd for C₃₃H₂₆N₂O₄: C, 76.9; H, 5.3; N, 5.4. Found: C, 76.8; H, 5.26; N, 5.48.

3e: 90%. Anal. Calcd for C₃₄H₂₈N₂O₄: C, 77.1; H, 5.5; N, 5.3. Found: C, 77.3; H, 5.46; N, 5.38.

3f: 88%. Anal. Calcd for C₃₆H₃₂N₂O₄: C, 77.5; H, 6.0; N, 5.0. Found: C, 77.1; H, 5.96; N, 5.08.

Typical Procedure for the Syntheses of Alternating Polyimides 6a–d. In a three-necked, round-bottomed flask, diamine **4** (2.269 g, 3.000 mmol), 6FDA (1.326 g, 3.000 mmol), and 0.5 g of isoquinoline were dissolved in 60 mL of *m*-cresol. The reaction solution was heated to 200 °C for 24 h, and during the course of the reaction, about 15 mL of *m*-cresol was distilled off. The mixture was then cooled to 100 °C and poured into 300 mL of methanol. The precipitated polymer was collected by filtration and washed with methanol several times. The polymer was then dissolved in TCE (150 mL) and precipitated by adding 100 mL of methanol dropwise into the stirred TCE solution. The sticky precipitate was then dissolved in 40 mL of TCE and precipitated into 300 mL of methanol. Polymer **6d** was filtered off, washed with methanol, and dried at 150 °C for 24 h under vacuum (5 mmHg). Yield: 3.29 g (91%).

Random Copolymer 7. It was prepared as for polyimides **6**, using dianhydride **1** (0.560 g, 1.427 mmol), dianhydride **5a** (0.562 g, 1.427 mmol), and diamine **4** (0.572 g, 2.854 mmol). Yield: 1.34 g (84%).

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX300 instrument using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. The UV–vis absorption spectra were recorded on a Cary 3 spectrophotometer. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Intrinsic viscosities were measured in concentrated sulfuric acid at 25 °C using an Ubbelohde dilution viscometer. The glass transition temperatures (*T*_g) were determined on a Seiko 220C DSC at a heating rate of 3 °C/min in nitrogen (200 mL/min) in oscillating mode. The onset temperatures for 5% weight loss of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25 to 800 °C at a heating rate of 10 °C/min in nitrogen. X-ray diffraction patterns were recorded for the as-prepared and annealed samples of **3f** and **6d**, using the Cu

Scheme 1. One-Step Solution Polymerization of Perylenetetracarboxylic Dianhydride (**1**) and Aliphatic Diamines **2a–f**

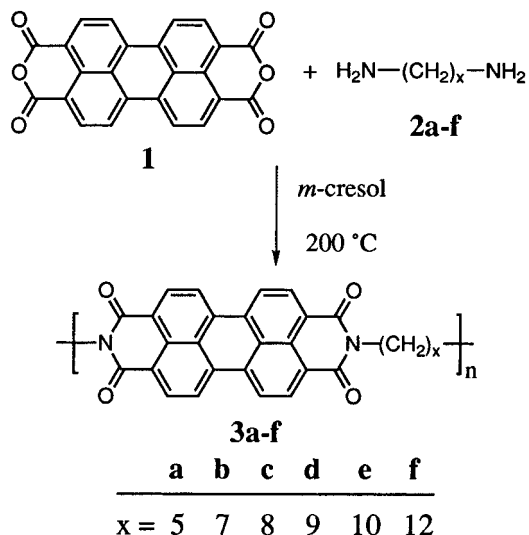


Table 1. Characterization of Homopolyimides 3a–f^c

polyimide	[η], dL/g ^a	<i>T</i> _d , °C ^b	H ₂ SO ₄	<i>m</i> -cresol	TCE
3a	0.47	402	+	±	–
3b	0.56	415	+	±	–
3c	1.06	451	+	±	–
3d	0.30	418	+	±	–
3e	0.80	451	+	±	–
3f	0.70	410	+	±	–

^a Intrinsic viscosities measured in concentrated H₂SO₄ at 25 °C.

^b Onset temperature for 5% weight loss in nitrogen. ^c Key: soluble (+), partially soluble (±), not soluble (–) at ambient temperatures (0.5 g/dL).

Kα radiation (λ = 1.5418 Å). A flat plate camera (W. Warhus Co., Wilmington, DE) was used for recording the patterns on film.

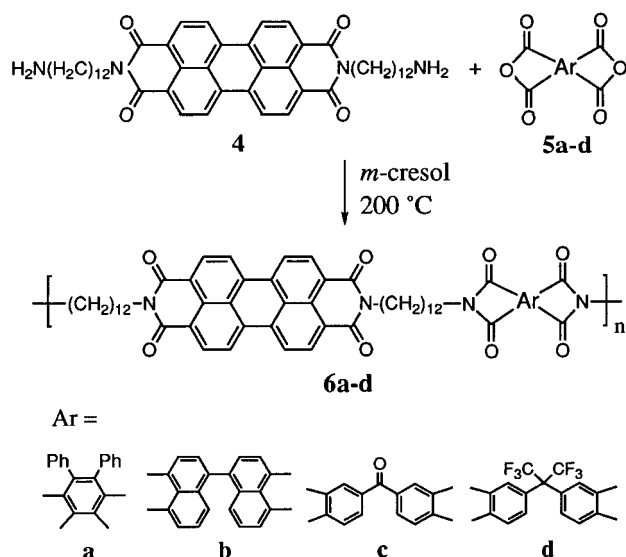
Xerographic Electrical Measurement. All measurements were done using a standard testing device² at the Xerox Research Centre of Canada. The polymers were dispersed in a currently used solvent (ca. 0.2 g in 8 mL of methylene chloride) using a ball-mill. These fine dispersion mixtures were coated on a metalized polyester substrate, dried at 135 °C for 20 min, and then cooled to room temperature to form a thin layer. After coating the charge transport layer (40% of a triarylamine in polycarbonate) and subsequent drying at 135 °C for 20 min, the coated film was then subjected to measurements of dark decay and photosensitivity.

Results and Discussion

Synthesis and Characterization. A series of linear aliphatic diamines (**2a–f**) were chosen for the preparation of homopolyimides with dianhydride **1** (Scheme 1). The polymerization was best carried out in *m*-cresol with a small amount of isoquinoline at 180–200 °C. The intrinsic viscosities of the polyimides ranged from 0.30 to 1.06 dL/g in concentrated sulfuric acid (Table 1). Completion of imidization was confirmed by IR, showing the absence of the anhydride's carbonyl peaks and the presence of the carbonyl peaks for the imide. It was found that the number of carbons in diamines **2** needs to be greater than 5 in order to obtain a partially soluble polyimide in *m*-cresol.

We recently synthesized two new dianhydrides, **5a**⁹ and **5b**,¹⁰ which were able to yield soluble rigid-rod-like polyimides. To further improve the processability or solubility, copolymerizations using these two dianhy-

Scheme 2. Synthesis of Alternating Copolyimides

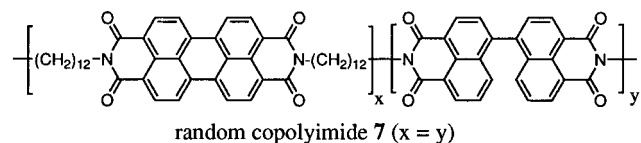


drides and commercial dianhydrides **5c** and **5d** were carried out. Random copolyimide **7** was first synthesized by one-step polymerization of dianhydrides **1** and **5b** in a 1:1 mol ratio and diamine **2f** in *m*-cresol. Indeed, the resulting polyimide was found to be more soluble than homopolyimides **3** but was not soluble enough to prepare a solution from common organic solvents for casting a tough film. This could be due to the formation of a short perylene-based block in the random polymer chain. On the basis of previous work on copolyimides,¹⁰ it was thought then that a perfectly alternating copolyimide should have much higher solubility.

To obtain perfectly alternating copolyimides according to the known approach,¹⁰ diamine **4** needs to be prepared first. It was prepared by adding dianhydride **1** into a large excess of diamine **2f** (10–20 mol equiv) in refluxing *m*-cresol in the presence of a small amount of isoquinoline. Under these conditions, no significant amounts of oligomers and polymers were formed. Purification of diamine **4** was achieved by simple extraction with hot *o*-dichlorobenzene. The structure of this diamine was confirmed by spectroscopic means and elemental analysis.

Polymerizations of diamine **4** with dianhydrides **5a–d** were carried out at 200 °C in *m*-cresol containing a small amount of isoquinoline (Scheme 2). No precipitation was observed during the polymerization. Four alternating copolyimides **6a–d** were obtained in high yields with intrinsic viscosities ranging from 0.50 to 0.88 dL/g in concentrated sulfuric acid (Table 2). Completion of imidization was confirmed by IR. All alternating copolymers were readily dissolved in *m*-cresol and concentrated sulfuric acid at room temperature. Copolyimides **6b** and **6d** were also soluble in TCE and partially soluble in chloroform, but still not soluble in methylene chloride, which is the solvent currently used for making a xerographic photoreceptor. Flexible, transparent, and tough films were then cast from the *m*-cresol solution of these copolyimides.

All polyimides synthesized were characterized by differential scanning calorimetry (DSC) and thermogravimetry (TG). Polyimides **3** and **6** were quite thermally stable in nitrogen, as indicated by the onset temperatures (T_d) for 5% weight loss ranging from 410

Table 2. Characterization of Copolyimides **6a–d** and **7**^c

polyimide	$[\eta]$, dL/g ^a	T_g , °C	T_d , °C ^b	<i>m</i> -cresol	TCE	CHCl ₃
6a	0.88	N/O ^d	478	+	–	–
6b	0.50	210	470	+	+	±
6c	0.56	N/O	451	+	±	–
6d	0.63	170	486	+	+	–
7	0.63	195	450	+	+	±

^a Intrinsic viscosities measured in concentrated H₂SO₄ at 25 °C. ^b Onset temperature for 5% weight loss in nitrogen. ^c Key: soluble (+), partially soluble (±), not soluble (–) at ambient temperatures (0.5 g/dL). ^d N/O: not observed.

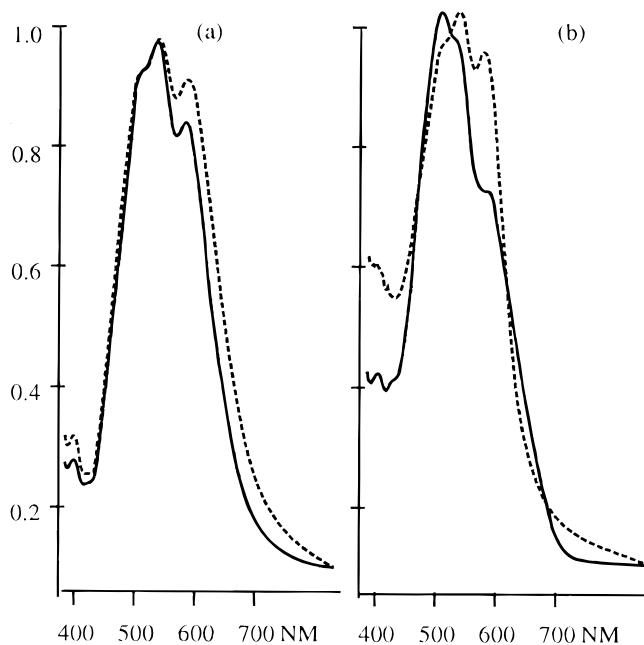


Figure 1. UV-vis absorption spectra of (a) **3f** and (b) **6d** in the solid state, before annealing (solid line) and after annealing at 320 °C for 2 h (dotted line).

to 486 °C. The glass transition temperatures of polymers **6** were in the range 170–210 °C by DSC (Table 2). In addition, the DSC traces of alternating copolyimides **6c** and **6d** displayed an endothermic peak at approximately 300 °C. This transition was observable in the repeated heating-cooling scans. Although the glass transitions of polymers **3a–f** were not detectable by DSC, their T_g values should be less than those of aromatic copolyimides **6** (e.g., 210 °C for **6b**). Therefore, these perylene-containing polyimides should be amenable toward an annealing process within a temperature window between their T_g values and decomposition temperatures.

For photoconducting pigments, it is known that the heat- or solvent-induced crystal packing can change the absorption spectrum and affect photogeneration efficiency and carrier mobilities.¹¹ Therefore, annealing was performed in an attempt to increase the crystallinity of the perylene-containing polyimides. Due to the alignment of the perylene units, the xerographic properties are expected to be improved. Polyimides **3f** and **6d** were subjected to annealing and characterized by UV-vis absorption and X-ray powder diffraction measure-

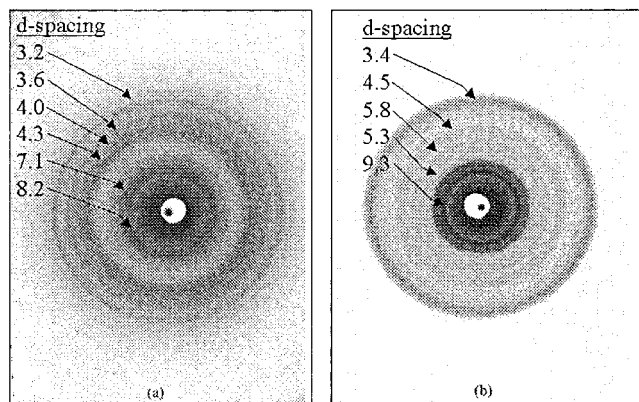


Figure 2. Wide-angle X-ray diffraction patterns of **3f**, (a) as prepared and (b) after annealing at 320 °C for 2 h.

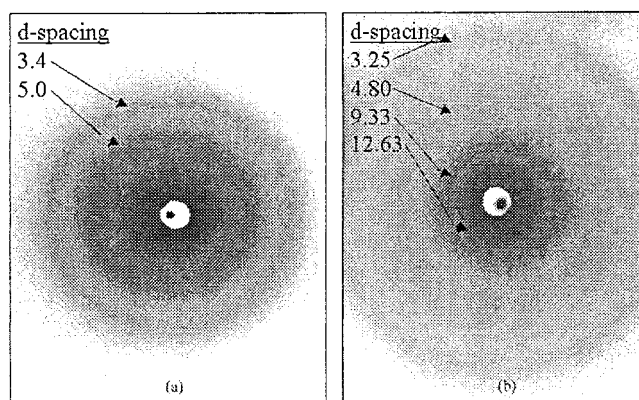


Figure 3. Wide-angle X-ray diffraction patterns of **6d**, (a) as prepared and (b) after annealing at 320 °C for 2 h.

ments. After annealing at 320 °C for 2 h, both **3f** and **6d** showed an increase in absorption at about 400 and 600 nm (Figure 1). In addition, the UV-vis absorption spectra of polyimide films were found to have a red-shift after annealing (Figure 1, dotted lines), indicating a higher degree of perylene overlapping. An increase in crystallinity was further supported by wide-angle X-ray diffraction data. Figure 2 shows the wide-angle X-ray diffraction (WAXD) patterns for **3f** before and after annealing. Although quantitative evaluation of the crystallinity was not performed, visual inspection shows that the crystallinity increases upon annealing and changes in the d spacings of the reflections are also noted. Figure 3 shows the WAXD patterns of **6d** before and after annealing. While the as-prepared material is mostly amorphous, crystallinity develops upon annealing. It should be noted that because of the copolymeric structure, the crystallinity of **6d** is significantly lower than that of **3f**. Whether the pattern shown in Figure 3 is indicative of a smectic arrangement needs verification.

Xerographic Electrical Characteristics. A typical xerographic process usually includes four steps: charge, delay, expose, and erase. A standard testing device containing a photoconductor was capacitively charged to high surface potential. After charging, the material loses some charge during a certain period of time, which is measured as dark decay (V/s). The device was then exposed to measured amounts of white light, and the reduction in voltage as a function of the light intensity was measured. The photosensitivity is expressed as $E_{1/2}$, the energy required to photodischarge half of the initial potential. A good photoconducting material

Table 3. Xerographic Electrical Characteristics

polyimide	photosensitivity $E_{1/2}$ (erg/cm ²)	dark decay (V/s)
3a	371	9.8
3c	268	8.8
3e	147	9.8
3f	104	23.8
3f^a	73	22.8
6a	82	17.4
6b	53	103.6
6c	80	17.2
6d	120	14
7	95	76

^a After annealing at 320 °C for 2 h.

should have a low dark decay (<50 V/s) and a high photosensitivity ($E_{1/2} < 20$ erg/cm²). Accordingly, dark decay and photosensitivity of several perylene polyimides were measured and compared.

Copolymers **6a–d** containing equal amounts of perylene dianhydride **1** and other dianhydrides **5a–d** displayed a moderate photosensitivity of 80–120 erg/cm² (Table 3). In comparison, homopolyimides **3a,c,e,f** showed relatively low photosensitivity ($E_{1/2} = 104$ –371 erg/cm²). After annealing at 320 °C for 2 h, polyimide **3f** showed much improved sensitivity ($E_{1/2} = 73$ erg/cm²) as compared to the "as-prepared" sample **3f** ($E_{1/2} = 104$ erg/cm²), seemingly due to an increase of crystallinity (Figure 2) and a higher degree of overlap of the perylene units (Figure 1). But, the study on a series of perylene bisimide pigments indicated that there is no relationship between the amount of overlap in the perylene crystals and the photosensitivity.¹² All polyimides measured except polymers **6b** and **7** showed a good charge-holding property, as their dark decay values were in a range 8.8–23.8 V/s. Among all polymers tested, alternating polyimides **6a** and **6c** had the best combination of sensitivity and dark decay. Furthermore, the latter two had a much lower dark decay (17 V/s) than that of a classical inorganic photoconductor (e.g., Se, 76 V/s).

Conclusion

Random and alternating copolyimides were found to be more soluble than perylene homopolyimides. Flexible, transparent, tough films can be cast from the *m*-cresol solution of alternating copolymers, but not methylene chloride, indicating the limitation of these polyimides as ideal binders. Two alternating perylene copolyimides **6a** and **6c** had the best combination of high photosensitivity and low dark decay, compared to other homopolyimides and copolyimides measured. An increase in crystallinity of these perylene polyimides upon annealing could lead to significant improvement of the photosensitivity.

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