Electron-Transporting Polyamides for Organic Photoreceptors

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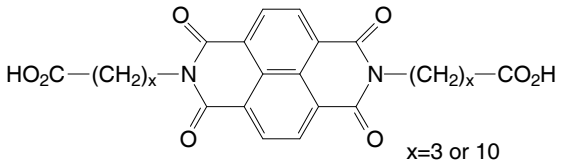
Abstract

*Negatively chargeable dual-layer organic photoreceptors (OPC) are typically prepared with an electrical (hole) blocking layer disposed between the conductive support and the charge-generation layer (CGL). The blocking layer provides an energy barrier to the injection of positive charges. In an electrophotographic charge/expose cycle, charge is generated in the CGL, and the OPC is discharged primarily by the transport of positive charge through the charge-transport layer to the negatively charged surface. Simultaneously, electrons in the CGL drift toward the grounded conductive layer. If the intervening blocking layer material is insulating, an undesirable residual charge will be produced. We have prepared hole-blocking layer polymers that transport electrons under an applied electric field. In these materials, naphthalene bisimide (**NB**) is the transport active moiety. This talk will discuss the synthesis and properties of high molecular weight polyamides with incorporated tetracarbonylbisimides. A desirable characteristic of such a blocking layer is that solvents used in the coating of subsequent layers do not attack it. These electron-transport active polyamides are soluble in mixed solvents, but are insoluble in chlorinated hydrocarbons or other solvents commonly used for coating other OPC layers. Because these blocking layers transport electronically, their function is substantially insensitive to humidity.*

Introduction

An office copier or laser printer uses a photoconductive thin film (photoreceptor) to convert an optical input into an electrostatic latent image on the film surface [1]. The bulk of the photoreceptor is usually a "molecularly doped polymer" consisting of electron acceptor or donor molecules dispersed in a polymer matrix that provides mechanical strength. Our current effort to incorporate electron transport agents in condensation polymers is based on earlier work [2]. The synthesis of the difunctional naphthalene bisimide (**NB**) monomers was reported with alcohol and phenol functional groups on the side chains for incorporation into polyesters. The polymers were used to form electron-transport layers in multilayer, positive-charging organic photoreceptors. These materials are soluble in chlorinated solvents and created by melt-phase polymerization.

More recently, we described modification of the polyesters for hole-blocking layers (BL) in negative-charging multilayer photoreceptors [3]. We now extend this work to polyamides made by incorporation into the polymer backbone of carboxylic acid functionalized 1,4,5,8-naphthalenetetracarbonyl-bis(imidoalkylenecarboxylate) (**NBX**), where X = 3 or 10 (Structure 1) [4].



Structure 1. *1,4,5,8-naphthalenetetracarbonyl-bis(imidoalkylenecarboxylate).* (**NBX**).

These **NB**-containing polyamides are useful as hole-blocking layers (BL) in negative-charging multilayer photoreceptors. The polymer is coated between the electrode layer (EL) and the charge-generation layer (CGL) to prevent undesired injection of positive charge from the electrode layer (Figure 1). The benefit of using an electron-transporting layer for this purpose is that negative charge in the generation layer is removed through this layer, preventing unwanted buildup of trapped charge with electrophotographic cycling.

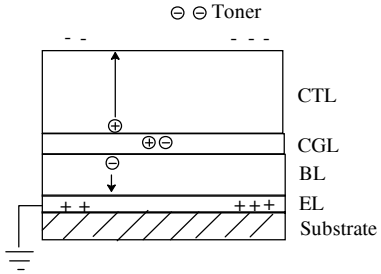


Figure 1*. Cross-section of negative charging photoreceptor.*

A requirement for this BL polymer is that it not be soluble in chlorinated solvents such as dichloromethane or 1,1,2-trichloroethane, as well as ketones and tetrahydrofuran. These nonpolar solvents are used to deposit the CGL of titanyl phthalocyanine pigment in a binder onto the barrier layer, and mixing of the two layers can lead to unfavorable electrical properties. A charge-transport layer (CTL) consisting of a hole-transport agent in a polyester/polycarbonate binder is coated on the CGL. The **NB** polyimides are not soluble in chlorinated hydrocarbons or the other commonly used solvents for coating photoconductor or charge-generation layers if a polar co-solvent such as ethanol is not also present.

Experimental

Polymer 1. Poly[2,2'-(ethylenedioxy)bis(ethylene)-co-piperazine-co-1,3,3-trimethylcyclohexane-1,5-methylene (10/25/65) decamethylene-co-1,4,5,8-naphthalenetetracarbonyl-

bis(imidopropylene)-co-1,4,5,8-naphthalenetetracarbonyl-bis(imido-11-undecamethylene)-co-octamethylene (25/10/60/5)]amide.

A mixture of 7.91 g (0.025 moles) of piperazonium dodecanedioate, 1.86 g (0.005 moles) of 1,3,3-trimethylcyclohexanemethylenediammonium sebacate, 1.48 g (0.01 moles) of 2,2'-(ethylenedioxy)bis(ethylamine), 10.22 g (0.06 moles) of 1,3,3-trimethylcyclohexanemethylenediamine, 4.38 g (0.01 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(3-carboxypropyl)imide, 38.0 g (0.06 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(11-undecanoic acid)imide contained in a polymerization flask equipped with a Claisen head and a nitrogen inlet tube is heated to 220°C under a nitrogen atmosphere to produce a dark burgundy-colored, homogeneous melt. The temperature is slowly raised to 280°C over several hours. Heating is continued until no further distillate is observed. A mechanical stirrer is introduced, and the flask is connected to a source of vacuum. The mixture is stirred under vacuum at 280°C for about two hours, or until the desired melt viscosity is achieved, then the product is allowed to cool to room temperature.

Polymer 2. Poly[piperazine-co 1,3,3-trimethylcyclohexane-1,5-methylene (20/80) decamethylene-co-1,4,5,8-naphthalenetetracarbonyl-bis(imido-11-undecamethylene)-co-octamethylene (20/50/30)]amide.

A mixture of 31.6 g (0.1 moles) of piperazonium dodecanedioate, 55.9 g (0.15 moles) of 1,3,3-trimethylcyclohexanemethylenediammonium sebacate, 42.6 g (0.25 moles) of 1,3,3-trimethylcyclohexanemethylenediamine, 158.5 g (0.25 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(11-undecanoic acid)imide is combined and subjected to substantially the same polycondensation profile and procedure employed for Polymer 1.

Polymer 3. Poly[piperazine-co 1,3,3-trimethylcyclohexane-1,5-methylene (25/75) decamethylene-co-1,4,5,8-naphthalenetetracarbonyl-bis(imido-11-undecamethylene)-co-octamethylene (25/70/5)]amide.

A mixture of 7.91 g (0.025 moles) of piperazonium dodecanedioate, 1.86 g (0.005 moles) of 1,3,3-trimethylcyclohexanemethylenediammonium sebacate, 11.92 g (0.07 moles) of 1,3,3-trimethylcyclohexanemethylenediamine, 44.38 g (0.07 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(11-undecanoic acid)imide is combined and subjected to substantially the same polycondensation profile and procedure employed for Polymer 1.

Polymer 4. Poly[piperazine-co 1,3,3-trimethylcyclohexane-1,5-methylene (20/80) decamethylene-co-1,4,5,8-naphthalenetetracarbonyl-bis(imido-11-undecamethylene)-co-octamethylene (20/75/5)]amide.

A mixture of 6.33 g (0.02 moles) of piperazonium dodecanedioate, 1.86 g (0.005 moles) of 1,3,3-trimethylcyclohexanemethylenediammonium sebacate, 12.77 g (0.075 moles) of 1,3,3-trimethylcyclohexanemethylenediamine, 47.55 g (0.075 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(11-undecanoic acid)imide is combined and subjected to substantially the same polycondensation profile and procedure employed for Polymer 1.

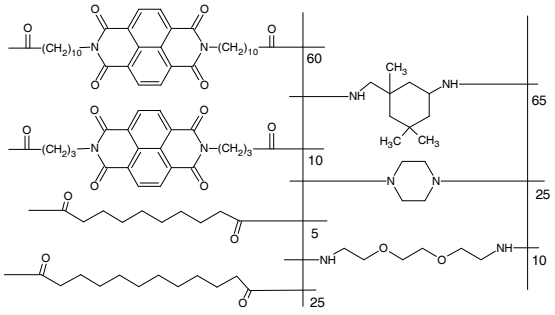
Polymer 5. Poly[2,2'-(ethylenedioxy)bis(ethylene)-co-piperazine-co-1,3,3-trimethylcyclohexane-1,5-methylene (5/25/70) decamethylene-co-1,4,5,8-naphthalenetetracarbonyl-bis(imido-11-undecamethylene)-co-octamethylene (25/70/5)]amide.

A mixture of 7.91 g (0.025 moles) of piperazonium dodecanedioate, 1.75 g (0.005 moles) of 2,2'-(ethylenedioxy)bis(ethylammonium)-sebacate, 11.92 g (0.07 moles) of 1,3,3-trimethylcyclohexanemethylenediamine, 44.38 g (0.07 moles) of 1,4,5,8-naphthalenetetracarbonyl-bis(11-undecanoic acid)imide is combined and subjected to substantially the same polycondensation profile and procedure employed for Polymer 1.

Results and Discussion

The **NB** containing polyamides were synthesized by melt polymerization [5]. Organic salts were prepared wherever possible to maintain the 1:1 stoichiometry between acid and amine. However, we found that the **NB** acids did not form 1:1 complexes with the desired amines, and therefore we often added the **NB** moieties as the free acids along with the appropriate amount of amine. The polymers were red in color and dissolved in chlorinated solvents with approximately 10–30% alcohol to give deep red solutions that could be readily characterized by standard analytical methods including molecular weight by size exclusion chromatography (SEC) (Table 1) and high-resolution nuclear magnetic resonance (NMR). An advantage of the polyamide melt synthesis is catalysts are not necessary for the polymerization, and this eliminates a source of contamination or unwanted doping of the electron barrier. The polymers were good film formers and could be easily coated for infrared (IR) analysis or as electrodes for photoreceptors and solar cells [6].

The structure of one of the more complex **NB** polyamides, **Polymer 1**, is shown in Structure 2. We found that good transport was obtained in layers where the **NB** content of the polymer was above 50 mol % of the acid component. In this structure both **NB3** and **NB10** were used to obtain a high level of loading of the transport agent while at the same time minimizing crystallinity that was found to inhibit electron transport [7]. Our early work employed phenylindane diacid as a co-substituent, which gave desirable properties for solubility of the polymers. However, because this monomer was not readily available commercially, competed with the **NB** diacid for content of the polymer, and could potentially interfere with the stacking of the **NB** units and inhibit electron transfer, other monomers were chosen for incorporation of desirable properties [8]. The isophorone diamine comprises a dimethyl-substituted cyclohexane ring with two chiral centers that helps prevent the chains from crystallizing, along with the cyclic diamine piperazine, which could be used to control the level of solubility of the polymers. The ether monomers were sometimes used to give the polymer greater flexibility, and the long chain alkylene diacids served to help control the polymer's physical properties as well as form stable salts with the diamines.



***Structure 2**. Structure of **NB** amide Polymer 1.*

Thermal characterization of the polymers was carried out by differential scanning calorimetry (DSC) (**Table 1**). The relatively high Tg of greater than 105°C is probably due to a combination of the stiff **NB** moieties and the hydrogen bonding that naturally occurs in polyamides. **Polymer 4** has the highest level of **NB** content at 75 mol % of the acid portion, and the crystalline melting peak was observed in all three thermal scans. **Polymer 5** has a high level of the ether that may lead to an enhanced tendency to crystallize. The molecular weights of the materials were broad and contained two distributions [9].

Table 1. Thermal Properties and Molecular Weights of NB Amides.

Polymer	Tg (°C)	Tm (°C)	Mn	Mw
1	106	–	34800	114000
2	112	–	39000	130000
3	111	–	44700	174000
4	115	166	38200	109000
5	106	159	37700	107000

One characteristic of the electron transport properties of the **NB** amides is the reversible reduction potential in the cyclic voltammogram (Figure 2). The **Polymer 1** was dissolved in dichloromethane/methanol $(75/52)_{vol}$ and tetrabutylammonium tetrafluoroborate was added as a supporting electrolyte. A glassy carbon disk (A = 0.071 cm^2) was the working electrode and a platinum wire served as a counter electrode. Potentials were recorded against the saturated calomel electrode (SCE). The reduction potential was –0.548 V. The side wave in the cyclic voltammogram could be due to the polymer being absorbed on the electrode surface. A blank solution prepared using the aliphatic polyamide Amilan™ 8000 did not show a reduction wave due to the absence of the electron-deficient aromatic **NB** moiety.

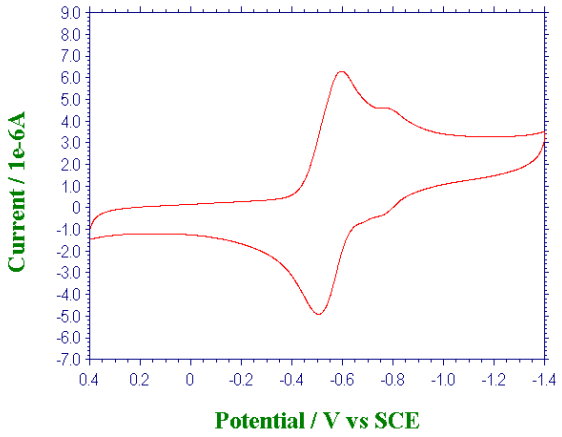


***Figure 2**. Cyclic voltammogram of **Polymer 1**.*

The rate of electron migration through the **NB** amide layer was measured using time-of-flight techniques. Two samples of **Polymer 2** were dip coated onto a nickel substrate from chlorinated solvents/alcohol and dried at 110°C. The 1- and 2-µm-thick films were vacuum coated with gold and the mobility measured as a function of the square root of the field (Figure 3). The mobility was found to vary inversely with the field and to have a value in the 10^{-5} cm^2/Vsec range. This is about the same mobility as hole-transport agents triarylamines, although they display an increasing mobility with field strength. The unusual inverse dependence of mobility with applied field has also been observed in hole transport and is believed to be a consequence of energetic and positional disorder [1].

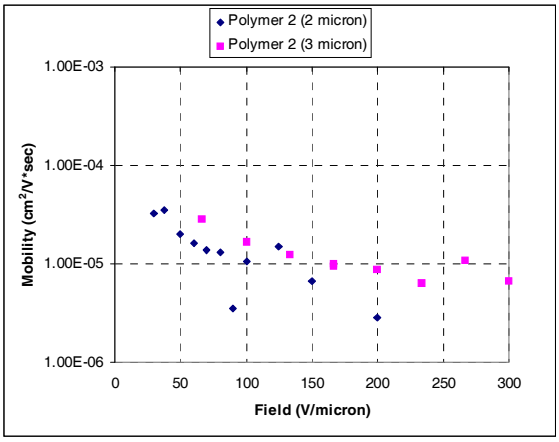


***Figure 3**. Electron mobility of **Polymer 2**.*

The transport of electrons through the polymer layers is thought to involve interactions between **NB** groups. Wide angle x-ray diffraction showed some level of order in all of the polymers. The 2-dimensional (2D) diffraction pattern of **Polymer 3** (Figure 4) is typical of the scattering of these "amorphous" materials. The haloes are diffuse, but comparison with the diffraction pattern of the **NB** monomer suggests that the ordering in the polymer is due to the **NB** moiety.

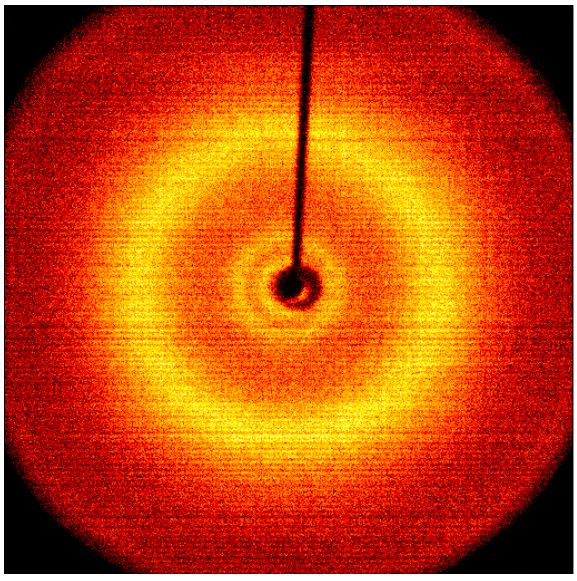


***Figure 4. Polymer 3** 2D x-ray diffraction pattern.*

The increase in order of the polymers with increasing **NB10** content is seen in the 1-dimensional (1D) diffraction comparison in Figure 5. **Polymer 2** with 50 mol % **NB10** of the acid function has only a faint contribution from the monomer. **Polymer 3** with 70 mol % **NB10** begins to exhibit two low-angle peaks of the **NB10** monomer as well as the diffuse pattern leading to the large peak. The crystalline peaks at the low angles are better defined in **Polymer 4**, which has 75 mol % of the acid monomer as **NB10**. We have found that this polymer does not transport charge as well as either of the other two, probably because of barriers caused by the onset of crystallinity.

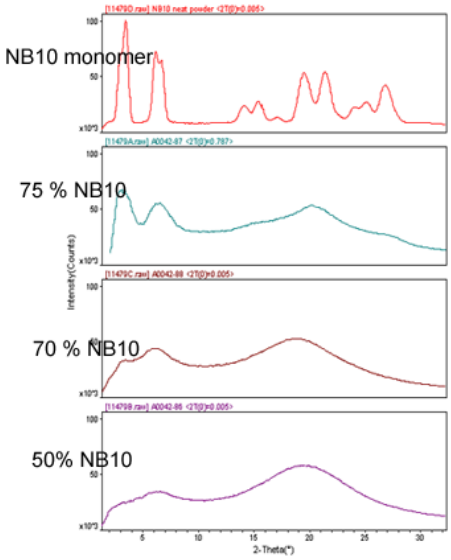


Figure 5. *Wide angle x-ray diffraction of* ***Polymer 2, Polymer 3****,* ***Polymer 4,*** *and the* ***NB10*** *monomer.*

Films of the polymers cast from solvents were sometimes brittle, but could be made tough by the incorporation of organic cosubstituents. The dynamic-mechanical spectrum showing the modulus as a function of temperature for **Polymer 5** is shown in Figure 6. The polymer begins to soften above 90°C, which is slightly lower than the Tg observed by DSC in **Table 1**. The polymer begins to flow at approximately 155°C, which is close to the melting temperature of the crystalline domains observed by DSC (Table 1). These factors are expected to be important for the photoreceptor, both during drying to remove the solvents from the barrier layer, and subsequent drying and curing of other layers with regard to mixing.

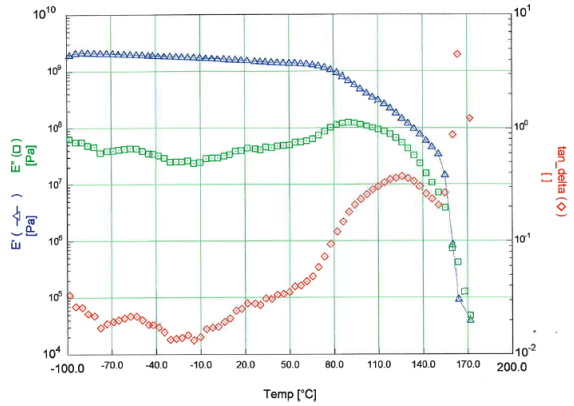


Figure 6. *Dynamic-mechanical spectrum of* ***Polymer 5****.*

Acknowledgments

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[8] Y. King and B. Bikson, Polymer, 43, 4709 (2002).
[9] Polystyrene equivalent molecular weights were obtained by SEC in 20/80 dichloroacetic acid/dichloromethane containing 0.01 M tetrabutylammonium acetate using three 7.5 mm by 300 mm Polymer Laboratories PLHFIP gel mixed-bed columns.

Biography

Wayne T. Ferrar is a member of the Graphics Communication Group at Eastman Kodak Company. He is a polymer chemist involved with the synthesis and characterization of acrylates, amides, esters, siloxanes, and phosphazenes for charge-transporting polymers in electrophotographic applications. He has also synthesized organic/inorganic composites for photographic and inkjet applications. Wayne received his doctorate under H. R. Allcock at Penn State University.