Photogeneration Efficiency Study of New Sol-gel Materials

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Abstract

This paper reports our studies of the preparation and characterization of novel xerographic photoreceptors with sol-gel based silsesquioxane polymeric charge transport layers. Photoreceptors have been prepared where the sol-gel layer is the sole transport layer (CTL) directly contacting the near-IR-absorbing charge generation layer (CGL). The sol-gel layers are novel in that they incorporate charge transport moieties covalently linked in a co-polymer, which is subsequently networked into the silsesquioxane matrix via the sol-gel process. We have investigated the photogeneration efficiencies of these photoreceptors and their dependence on sol-gel composition.

Introduction

In the electrophotographic process the photoreceptor is subjected to a variety of physical and chemical abuses. The surface layer of an organic photoreceptor is typically a charge transport layer (CTL), which is an organic polymer doped with high loadings (40-50 wt%) of charge transport material (CTM). The CTL is relatively soft, so that cleaning, by blade or brush, causes scratches and abrasive wear. Unintended contacts of the surface with sharp objects may result in scratches that necessitate immediate photoreceptor replacement. The photoreceptor surface is also relatively permeable and its components are reactive towards the ozone and nitrogen oxides generated during corona charging. After extended exposure to such chemicals, the electrophotographic characteristics may degrade to the point where image defects become objectionable. Organic photoreceptors are also susceptible to photochemical damage from ultraviolet radiation emitted from the corona discharge or from exposure to room light. As a result of these factors, the lifetime limit of an organic photoreceptor is on the order of one hundred thousand cycles. By contrast, a lifetime of one million cycles is typical of the much harder amorphous silicon and arsenic triselenide photoreceptors. Extensive efforts have been devoted to the stabilization of photoreceptors to such abuses.

Overcoating the photoreceptor with a tough and chemically impervious layer is one approach that has been utilized to extend the practical photoreceptor lifetime. Overcoats from silsesquioxane polymers have been widely reported.[1-12] The organic silsesquioxane overcoats are normally prepared by the sol-gel process.[13-15] In general, relative to the typical organic polymer based CTL these overcoats have higher hardness, better scratch and abrasion resistance, lower chemical permeability and better solvent resistance. However, silsesquioxane overcoats may have some drawbacks. First, because silsesquioxane polymers are not in general particularly compatible with organic photoreceptor materials, the overcoats might not bond well and easily peal off of the underlying layer. Second, the organic silsesquioxane overcoats are usually brittle and crack with bending and/or mechanical stress. Third, in the absence of charge transport properties, the silsesquioxane overcoats can build up a high residual voltage during the electrophotographic process.

We discussed the design and synthesis of a series of novel copolymers with covalently bonded charge transport moieties and silane groups in a previous paper.[16] Through a silsesquioxane sol-gel process, the obtained silsesquioxane matrix provides a hole transporting material that can be utilized as a CTL or as a protective overcoat on a dual layer photoreceptor. To simplify the system and study directly the hole transport properties of our silsesquioxane materials, we prepared the photoreceptors with a sol-gel charge transport layer as the only transport layer. We report in this paper the systematic characterization of the field dependence of charge generation of our novel hole transport sol-gel materials. The dependence of photogeneration efficiency on the composition of the sol-gel layers was investigated.

Experimental

The synthesis of the charge transport copolymers, poly[di(*p*-tolyl)amino styrene-co-methacryloxypropyl trimethoxysilane] (poly(DTAS-MATMS)), and their application in photoreceptor films through a sol-gel process were discussed in a previous paper.[16] The preparation of the silsesquioxane solutions with those copolymers and methyltrimethoxysilane (MTMS) were catalyzed by acetic acid and Ludox LS colloidal silica.[13,16]

The obtained silsesquioxane solutions were coated as the charge transport layer on the near infrared sensitive electrophotographic substrates, which were made from the solvent coating of a 0.5 micron of charge generation layer

(CGL) consisting of oxotitanium phthalocyanine pigments and polyester ionomer on a poly(ethylene terephthalate) film with a vacuum coated conductive layer of nickel. The thickness of the silsesquioxane coating was controlled by the gauges of coating knifes. The overcoated films were cured in an oven at 80 °C for 24 hours. Most of the films after curing are smooth, transparent and free of obvious defects.

The weight percentage of charge transport material moieties, DTAS, in the coatings was calculated based on the coating solution formulation and the amount of charge transport repeat units in the copolymers. The thickness of the sol-gel coating was determined by a 2500X cross-section photomicrograph.

Photogeneration efficiencies were determined by the emission limited photo-discharge technique. The photoreceptor sample is charged to the desired surface potential, and then exposed from the "front" (through the CTL). The surface potential is monitored continuously before and during the photo discharge. The light source is a shuttered xenon lamp and monochromater at 775 nm. The irradiance is determined by placing a calibrated silicon photo-detector in the light beam at the film plane. The photogeneration efficiency is the ratio of the number of the generated free electron-hole pairs to the number of absorbed photons. If it is assumed that recombination and deep trapping are absent in the system, the photogeneration efficiency can be calculated as:

$$\eta = -\frac{\varepsilon\varepsilon_o}{LIe}\left(\frac{dV}{dt}\right) \tag{1}$$

where ε is the dielectric constant, ε_o the permittivity of free space, *e* the elementary charge, L the sample thickness, I the incident photon intensity (photons/cm^{2}sec) and dV/dt the rate of photoinduced potential discharge (volts/sec).[17,18] In our experiment, the photo-discharge rate was measured tangentially at the onset of exposure (or very shortly thereafter), $(dV/dt)_{V_o}$, so that the decrease in field during the exposure can be neglected. The photogeneration efficiencies were calculated directly from the photon intensity of the light source and not corrected for the light absorption of the photoreceptor films.

Results and Discussion

The chemical structure of charge transport copolymers, poly(DTAS-MATMS) is illustrated in Figure 1. After the sol-gel process, the solutions containing synthesized copolymers and MTMS were coated on the electrophotographic substrates as the only CTL layer and the electrophotographic properties of these films are directly related to the chemical structures and properties of the copolymer systems.

A typical low intensity continuous exposure discharge curve of a charge transport polymer film is shown in Figure 2. The photo-discharge occurs with little residual potential. The rate of discharge was measured from the slope of the onset of exposure, $(dV/dt)_{V_o}$. Substituting the values of ε, L and I into Equation 1 yields the photogeneration efficiency at the initially applied field.

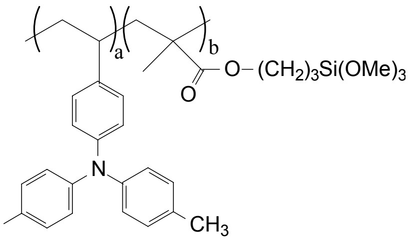

Figure 1. Chemical structure of charge transport copolymer.

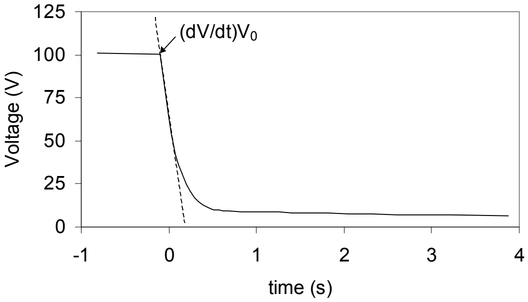

Figure 2. Photo-discharge curve of a photoreceptor with a charge transport layer based on poly(DTAS-MATMS).

The dependence of photogeneration efficiencies on the film thickness and light intensity was studied to verify the absence of recombination and deep trapping, which are the essential assumptions for Equation 1. The photogeneration efficiencies of a film with 33% DTAS were studied under a wide range of exposure intensity. Figure 3 shows that the discharge slopes $(dV/dt)_{V_o}$ increase linearly with the light intensity, which yield relatively constant photogeneration efficiencies of 0.37. Figure 4 shows the field dependence of the quantum efficiencies for a photoreceptor films with 48% DTAS. The results indicate that the photoreceptor films follow the same field dependent curve of the photogeneration efficiency regardless of the different coating thickness. The absence of light intensity and coating thickness dependence illustrates that the photogeneration of these charge transport sol-gel films is emission-limited and the deep trapping and recombination of charge can be ignored.

The photogeneration efficiencies of the sol-gel films were found to be CTM concentration dependent as shown in Figure 5. The higher the CTM concentration in the films, the higher the efficiencies. The concentration dependence becomes less significant when the CTM concentration reaches a certain level. In the films based on poly(DTAS-MATMS), the critical CTM concentration is about 20%.

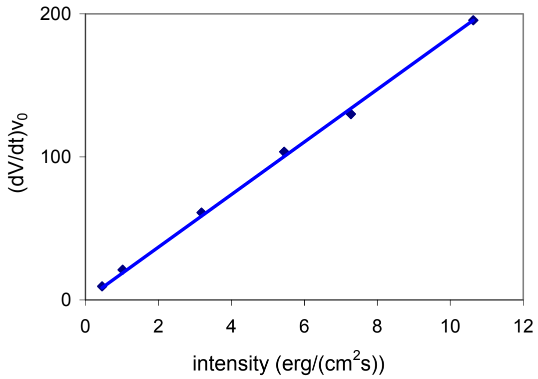

Figure 3. Relation between (dV/dt)Vo and light intensity (sample thickness: 2.2 µm; DTAS concentration: 33.0%; applied fields: 4.5x105 V/cm)

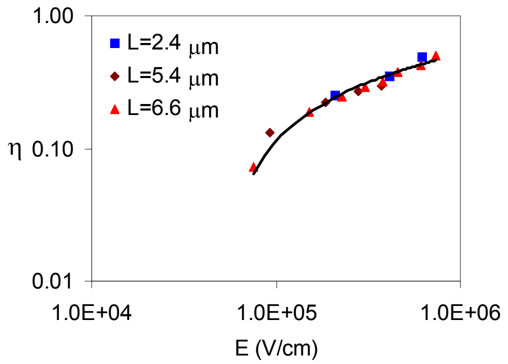

Figure 4. Field dependence of the photogeneration efficiencies of films with different thickness.

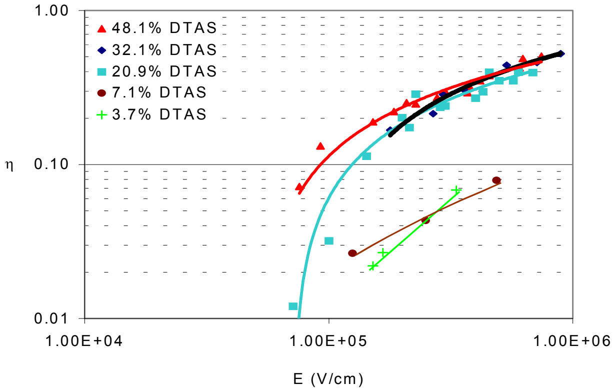

Figure 5. Efficiency dependence on the concentration of DTAS moieties.

Our results have similarities to the data reported by Molaire *et al.* for the films using typical triarylamine CTM in a polymer binder.[18] The maximum efficiency observed in our silsesquioxane based transport layers is about 70% of that observed with the use of a standard, doped polymer, transport layer.[18] This may be a reflection of decreased contact between the pigment surface and the hole transport material in these systems. This observation provides an opportunity to tailor the generation efficiency of a photoreceptor for a given process without adversely affecting charge transport through the CTL.

Conclusion

We have described the preparation of hole transport layers with a sol-gel process utilizing copolymers in which one component has a covalently bound hole transport moiety. Photoreceptors prepared with the sol-gel CTL using the polymers described here exhibit some noteworthy characteristics. First, photo-discharge occurs with little residual potential. This demonstrates that charge is generated and transports without significant transport limitation. Furthermore, the quantum efficiencies and field dependence are similar to the standard near-infrared sensitive photoreceptors. The maximum quantum efficiency is 0.63 (corrected for the light absorption of the photoreceptor at 775nm) and depends on the concentration of hole transport moiety in the sol-gel CTL. The application of sol-gel CTLs opens new opportunities in OPC formulation which may take advantage of the superior hardness and scratch resistance of the silsesquioxane based CTL.

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Biography

Xin Jin received his Ph.D. in Polymer Sciences and Engineering from the University of Massachusetts at Amherst in 2000. Since then he has worked In Heidelberg Digital LLC as a Research Scientist. His work has primarily focused on the research and development of polymer materials applied in photoreceptors and other electrophotographic areas. He is a member of the American Chemical Society.