

Novel Sol-gel Materials with Charge Transporting Properties

Xin Jin,[▲] David S. Weiss[▲] and Louis J. Sorriero

Heidelberg Digital L.L.C., Rochester, New York, USA

Wayne T. Ferrar[▲]

NexPress Solutions LLC, Rochester, New York, USA

A series of novel copolymers having components with hole transport ability and silane functionality have been synthesized. These copolymers were prepared by radical polymerization. Through a sol-gel process with methyltrimethoxysilane, solutions of the copolymers were coated to form the hole transport layer of an organic photoreceptor. These hole transport active silsesquioxane layers were coated as either a charge transport layer (CTL) on a charge generation layer (CGL) or a protective overcoat on a CTL. The electrophotographic and scratch resistant properties of the photoreceptors prepared with these sol-gel layers are described.

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Introduction

Organic polymers are used for charge transport in devices such as organic light-emitting diodes (OLED) and organic electrophotographic photoreceptors or photoconductors (OPC). In OLEDs charge is injected from an electrode into a charge transporting layer, in an OPC the charge is photogenerated and subsequently injected into the charge transport material dissolved in, or a functional part of, an organic polymeric material which serves as the binder. In these devices the aim is for charge to be transported, in the absence of trapping, from the site of injection to the counter electrode, driven by the applied field.

In the electrophotographic process the photoreceptor is charged and image-wise exposed. The charge transport layer (CTL) in most organic photoreceptors is a polymer molecularly doped (40-50% by weight) with a charge transport material. In the electrophotographic process this surface is subjected to a variety of physical and chemical abuses and is easily damaged. Extensive efforts have been devoted to the stabilization of photoreceptors to such abuse. One approach has been to "toughen" the CTL by selective doping, choice of binder polymer, use of a hole transport active polymer, etc. Another approach is the addition of an overcoat layer.¹⁻⁴

Overcoats must bind well to the underlying photoreceptor materials, be flexible and resist cracking in the electrophotographic process, and transport charge. Overcoats of silsesquioxane polymers have been utilized as

abrasion resistant overcoats,^{5,6} including overcoats for organic photoreceptors. Such organic silica overcoats are normally prepared by the sol-gel process.⁷⁻⁸ Silsesquioxane overcoats for organic photoreceptors are disclosed in many patents and in the open literature.⁷⁻¹² The protection of organic photoconductors using an overcoat comprising various polysiloxane mixtures in a polycarbonate resin has also been reported.¹³

The incorporation of charge transport materials (CTMs), such as tertiary arylamines, into silsesquioxane polymers for the purpose of transporting holes has been detailed in a series of patents.¹⁴⁻¹⁸ These patents employ a silane that has been covalently bonded to the phenyl ring of a tertiary amine through a non-hydrolyzable Si-C bond. Other synthetic pathways used are to prepare triarylamines with trialkoxysilane moieties attached through a Si-C bond.¹⁷ The resulting trialkoxysilyl-substituted triarylamines are coated as protective overcoats containing commercially available silicone hard coat materials. Recent articles in the chemical literature have compared sol-gel networks, including silsesquioxanes, that have useful moieties such as organic dyes attached to the siloxane network through non-hydrolyzable Si-C bonds and the equilibrium control addition through Si-O-C. For example, Bellmann et al. reported the incorporation of the functional moieties such as fluorinated tertiary arylamines and trimethoxyvinylsilane into polymer chains.¹⁸ However, due to the low reactivity of trimethoxyvinylsilane in radical polymerization, the percentage of the silane moieties in the copolymers was limited. Schneider et al. claimed that high quantities of perylenes could be incorporated into sol-gel networks by first coupling the dye to the silane and then forming the network.¹⁹ Alternatively, a dye can be incorporated in the sol-gel formation process as well.²⁰⁻²³

In general, there are several drawbacks for those reported silsesquioxane overcoats. First, because the silsesquioxane polymers are not sufficiently compatible

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▲ IS&T Member

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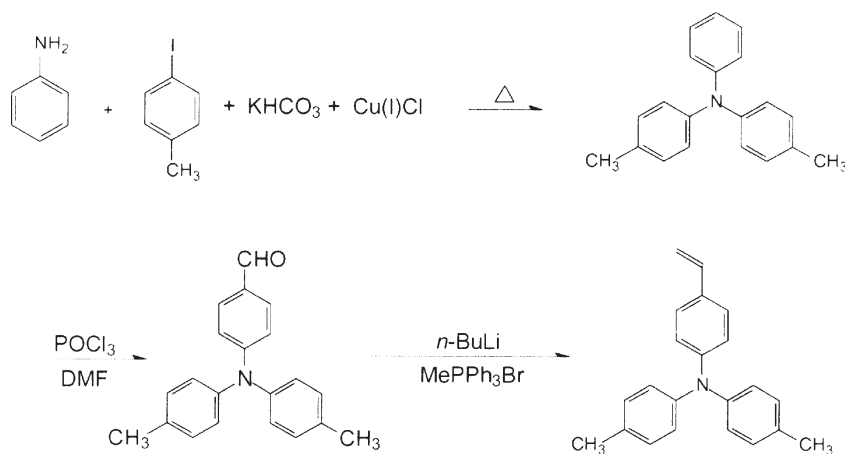


Figure 1. Preparation of di(p-tolyl)amino styrene (DTAS).

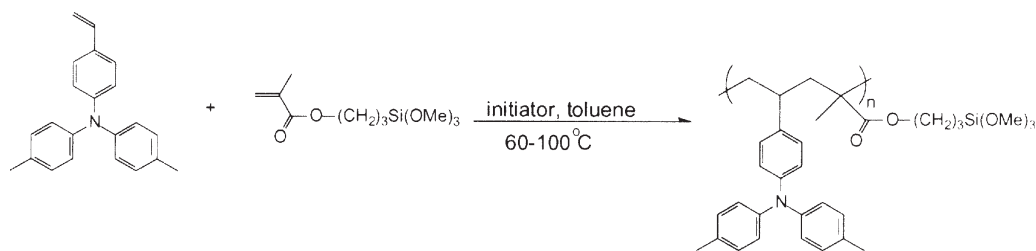


Figure 2. Radical polymerization of the functional monomers.

with organic photoreceptor materials, the overcoats are not bound well with photoreceptors and easily peel off. Second, the organic silicone overcoats are usually brittle and crack with bending and/or mechanical fatigue. Third, due to the lack of charge transport properties, the silsesquioxane overcoats can build up high residual voltage during the electrophotographic process. Many modifications of the silsesquioxane overcoats have been developed, but very few could overcome all of those weaknesses.

In this article, we report the design and application of novel silsesquioxane materials as hole transporting layers in organic photoreceptors.²⁴ In our approach a copolymer is prepared with one monomer having a hole transport functionality and the other having a hydrolyzable alkoxy silane functionality. The former provides hole transport characteristics and the latter a site for cross-linking in the formation of a silsesquioxane network.

Experimental

The synthesis of transporting monomers, preparation, characterization and application of the copolymers, are listed as follows. All chemicals in the synthesis, except those described specifically, were obtained from Aldrich Chemical Co. and used directly without purification.

Synthesis of Charge Transport Monomer, Di(p-Tolyl)Amino Styrene (DTAS)

The scheme for synthesis of the charge transport monomer is shown in Fig. 1. The purified product was obtained as a white crystal solid from above procedure. Melting point: 69-71°C. Elemental analysis: C: 88.67; H: 7.10; N: 4.63 (theoretically: C: 88.25; H: 7.07; N: 4.68).

The other monomer, methacryloxypropyl trimethoxy-silane (MATMS), was obtained from Aldrich Chemical and used as received.

Synthesis and Characterization of Organic Transporting Copolymers

Under an argon atmosphere, the silane and charge transporting monomer mixture with predetermined molar ratio was dissolved in anhydrous toluene. The radical initiator was then added to the solution. The reaction process is shown in Fig. 2. After the solution was heated to 60 – 100°C for 20 hours, the contents were cooled to room temperature and precipitated into methanol. The polymer was collected by filtration, washed with hexane several times, and dried under vacuum overnight.

The molecular weights of isolated polymers were analyzed by size-exclusion chromatography (SEC) in uninhibited tetrahydrofuran and the relative ratio of the functional groups was measured by Varian Mercury 300 MHz ¹H NMR. The glass transition temperatures of polymers were determined by TA Instrument DSC 2920 (Differential Scanning Calorimeter). A Model CHI660 electrochemical analyzer (CH Instruments, Inc., Austin, TX) was employed to carry out the electrochemical measurements with a regular platinum disk electrode (1 mm diameter) and an ultramicroelectrode (25 μm) (Bioanalytical Systems, Inc.). Platinum wire served as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. Methylene chloride containing 0.1 M TBABF₄ (tetrabutylammonium tetrafluoroborate) was used as a supporting electrolyte. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were

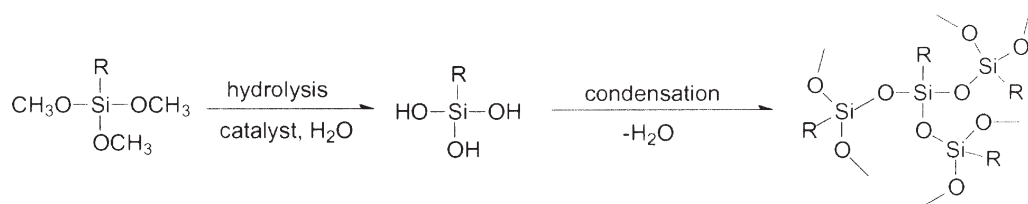


Figure 3. Illustration of the sol-gel process.

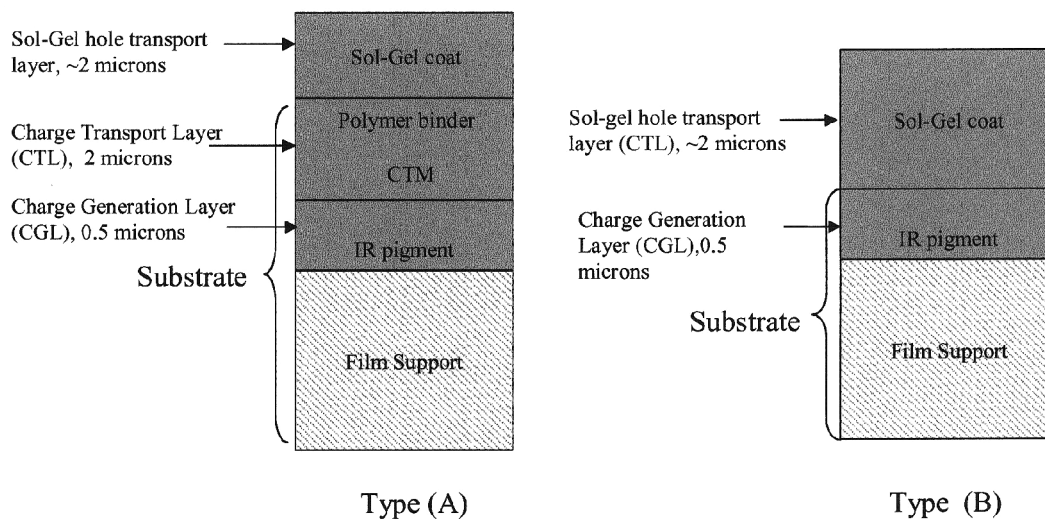


Figure 4. Structures of sol-gel overcoated photoreceptors: (A) sol-gel layer as protective overcoat over the CTL; (B) sol-gel layer as CTL on the top of the CGL.

used to determine the oxidation potentials, E_{ox}^0 which were estimated by averaging E_{pa} (anodic peak potential) and E_{pc} (cathodic peak potential).

Sol-gel Solution Preparation

The sol-gel solutions were prepared by the acidic hydrolysis and condensation of the copolymers with methyltrimethoxysilane (MTMS) as shown in Fig. 3.^{5,9,10} For comparison, a sol-gel solution without transporting copolymer was prepared with only methyltrimethoxysilane. R represents either a methyl group from MTMS or an alkylene group from the repeat unit of the transporting copolymers.

Coating of Sol-Gel Solution on the Photoreceptor Substrates

Two substrates, A and B, were used for the sol-gel overcoats. Substrate B is a CGL (0.5 micron) of a near-infrared sensitive pigment in a polymeric binder. Substrate A is the same CGL with a 2 micron conventional CTL. Both were on a poly(ethylene terephthalate) (7 mil) substrate with a conducting Ni layer. The sol-gel coated multi-layer photoreceptor films are illustrated in Fig. 4.

Electrophotographic Characterizations

The thickness of the sol-gel coating was determined by the cross section image of the electrophotographic film, which was cut with an American/Optical Spencer microtome mounted on a glass slide with a drop of mounting media. The image was viewed using Koehler

(transmitted light) illumination and then captured (using Image Pro Plus software) on a Jenaval microscope with a Hitachi HV-C20 3CCD video camera, 1X zoom lens and a GF Planapochromat HI 100x/1.35 objective. Low intensity continuous exposure was used to evaluate the electrophotographic characteristics. This was carried out by charging the photoreceptor sample to -100 V surface potential and then exposing through a "transparent" surface reading voltmeter probe. The surface potential was monitored continuously before and during the photodischarge. The residual voltages were determined after a 15 sec exposure (10 erg/cm^2 at 775 nm).

The scratch resistances of the photoreceptor films were measured by a nanoscratch experiment. A CSEM Nanoscratch Tester equipped with a 136 degree conical, 3 micron radius diamond stylus was used to generate scratches on the films under a 3 mN constant load. The resulting depths of the scratches, when visible, were determined using Digital Instrument DI 3000 Scanning Probe Microscopy with tapping mode.

Results and Discussion

The copolymers containing both silane and charge transport groups were synthesized through radical polymerization. A ^1H NMR spectrum of poly(DTAS-MATMS) is shown in Fig. 5. There are no impurity peaks, such as those from residual monomers and solvents, in the spectrum. The relative ratio of the triphenylamine and silane functional groups in the polymer chains was calculated based on the peak integration in aromatic region of 6.5 – 7.5 ppm and all other peaks below 5.0 ppm.

TABLE I. Copolymerization of DTAS and MATMS

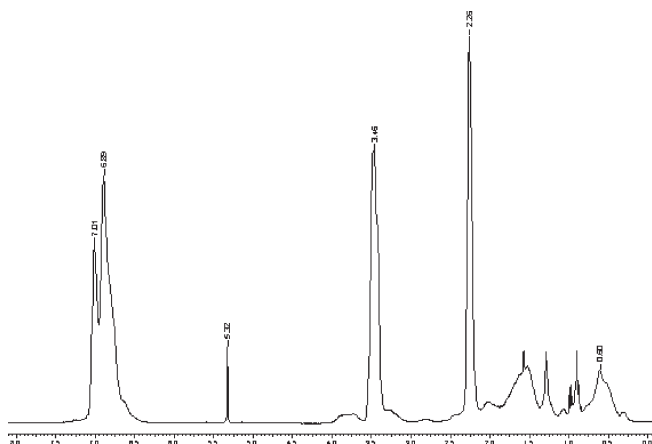
polymer	feed ratio (mol %) DTAS/MATMS	copolymer composition DTAS/MATMS (mol %)	T_g (°C)	M_n	M_w	E_{ox}^0 (V)
P1	5/95	6.1/93.9	-22.4	22200	49000	-
P2	10/90	12.1/87.9	-18.0	22700	63000	-
P3	25/75	37.3/62.7	51.4	23600	41700	-
P4	50/50	59.8/40.2	79.3	23500	40200	0.960
P5	75/25	79.5/20.5	110.3	28800	101000	0.960

DTAS: di(p-tolyl) aminostyrene; MATMS: methacryloxypropyl trimethoxysilane.

TABLE II. Photoreceptor Films from Sol-Gel Process and the Sensitometric Properties

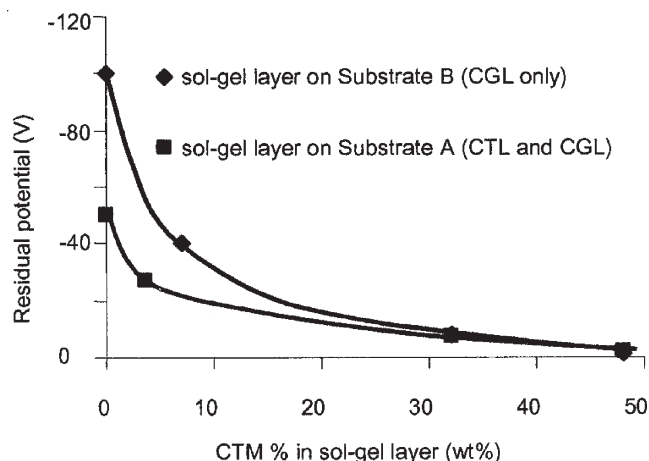
sample	substrate	polymer (wt)	polymer /MTMS Ratio CTM	% in sol-gel (wt %)	sol-gel thicknessresidual (μ m)	voltage (-V)
Control 1*	A	N/A	No overcoat	N/A	0	0
Control 2	A	N/A	0:1	0.0	1.8	50
A1	A	P1	1:1	3.7	1.2	27
A2	A	P4	1:1	32.1	1.6	7
A3	A	P3	1:0	41.8	2.0	2
A4	A	P4	3:1	48.1	1.8	2
Control 3	B	N/A	0:1	0.0	1.4	100
B1	B	P2	1:1	7.1	1.2	40
B2	B	P4	1:1	32.1	2.8	8
B3	B	P3	1:0	41.8	2.8	1
B4	B	P4	3:1	48.1	1.8	1

*: Control 1 is the Substrate A without any overcoat.

**Figure 5.** ^1H NMR spectrum of poly(DTAS-MATMS).

The copolymerization results of poly(DTAS-MATMS) with different comonomer ratios are shown in Table I. The data indicate that the reactivity of DTAS is slightly higher than MATMS. Due to the relatively bulky structure of DTAS, which limits the chain movement, the greater the percentage of DTAS in the polymer, the higher the glass transition. The oxidation potential of the poly(DTAS-MATMS), 0.96 V, is suitable for the electrophotographic CTL application.

Table II lists the photoreceptors, the sol-gel characteristics, and the residual potentials. With either substrate A or B the higher the content of charge transporting monomer in the sol-gel coating the lower the residual potential (Fig. 6). The CTM concentration in the sol-gel films can be adjusted by using the copolymers with different CTM compositions, such as P1-P5,

**Figure 6.** The dependence of residual potentials on the CTM concentration in the sol-gel layer.

or by using the same copolymer but with various combinations of the small molecule silane, MTMS. It was found that the photoreceptor films behave similarly regardless of the methods to control the CTM concentration, for example, A3 vs. A4 and B3 versus B4.

As shown, photoreceptors with sol-gel coats of the copolymer on CTL or CGL substrates, such as Sample A3, A4, B3 and B4, exhibited almost 100% photodischarge relative to the photoreceptor of Control 1 (no overcoat). In contrast, the sol-gel overcoat with only MTMS but no charge transport polymers (Control 2 and 3) exhibited no photodischarge through the sol-gel layers.

The electrophotographic properties under low humidity condition were characterized by low intensity continuous exposure experiment as well. The photoreceptor

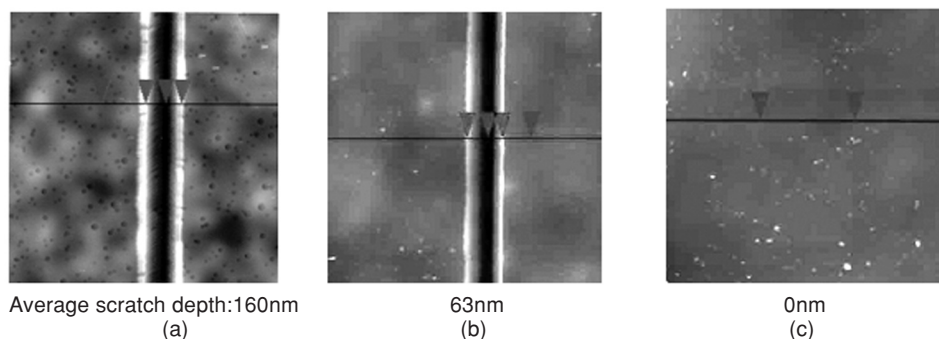


Figure 7. Scanning Probe Microscopy pictures of nanoscratch results. (a): Control 1, Substrate A without overcoat; (b): Sample A2; (c): Sample A1.

TABLE III. Low Intensity Continuous Exposure Results Under Near-Zero Humidity.

sample	polymer	CTM % in sol-gel (wt %)	- Vtoe (V) (ambient RH)	- Vtoe (V) (~ 0 % RH)
A1	P1	3.7	27	75
B1	P2	7.1	40	80
A2	P4	32.1	7	8
B2	P4	32.1	8	2

films were purged with pre-dried air overnight inside the chamber of the low intensity continuous exposure equipment. The relative humidity under this condition was close to zero.

The photodischarge results from low intensity continuous exposure experiments were achieved following the same method described above. Under this low humidity condition, the discharge data in Table III show that the photoreceptor films based on the new charge transporting copolymers with suitable amount of CTM units are not sensitive to humidity and give good discharge and low toe voltages at near zero humidity. Samples A1 and B1 are sensitive to humidity because there is not enough CTM in those films to provide efficient charge transport. These results indicate that the charge transporting in our sol-gel films is exclusively through electronic transport, which is conducted by the charge transport groups in our copolymer systems. Preliminary time-of-flight photocurrent measurement yields that the mobility of the charge transport sol-gel films is about $3.2 \times 10^{-5} \text{ cm}^2/(\text{Vs})$ at the field of $3 \times 10^5 \text{ V/cm}$, which is similar to the values generally obtained for the small molecule CTM, such as triarylamine, doped hole transport materials.

The scratch resistances of the photoreceptor films were determined by the nanoscratch method. The data indicate that the sol-gel coatings exhibit improved scratch resistance over the unprotected photoreceptor films as shown in Fig. 7. It is found that the lower the CTM concentration in the copolymers, the better the scratch resistance. These sol-gel films provide a practical approach to improve the lifetime of the commercial photoreceptor products without compromising the sensitometric requirements.

Conclusion

This study has demonstrated that the copolymerization of charge transport and silane monomers provides a practical approach to combine and tailor different prop-

erties into one polymer system. The silsesquioxane copolymers which have been developed represent a novel class of materials. They have good electrophotographic and mechanical properties. The sol-gel photoreceptors provide a practical approach to improve the lifetime of commercial photoreceptor products without compromising the sensitometric requirements. The novel silsesquioxane matrix provides a hole transporting material which can be utilized as a CTL or as a protective overcoat on a dual layer photoreceptor. The potential applications of these copolymers are as the charge transport layers for organic light-emitting diodes and electrophotographic photoreceptors. Δ

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