Novel Sol-gel Materials with Charge Transporting Properties

Xin Jin[1], Wayne T. Ferrar[2], David S. Weiss[1], and Louis J. Sorriero[1]
[1]Heidelberg Digital L.L.C., Rochester, New York
[2]NexPress Solutions L.L.C., Rochester, New York

Abstract

A series of novel copolymers having components with hole transport and silane functionality have been synthesized. These copolymers were prepared by radical polymerization. Through a sol-gel process with methyltrimethoxysilane, solutions of the copolymers with 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 properties of photoreceptors prepared with these sol-gel layers were described.

Introduction

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 silicone 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.[7-11] The protection of organic photoconductors using an overcoat comprising various polysiloxane mixtures in a polycarbonate resin has also been reported.[12]

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.[13-15] These patents employ a silane that has been covalently bonded to a 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.[16] 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.[17] 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.[18] Alternatively, a dye can be incorporated in the sol-gel formation process as well.[19-22]

In this paper, we report the design and application of novel silsesquioxane materials as hole transporting layers in organic photoreceptors. 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

A. Synthesis of charge transport monomer, di(p-tolyl)amino styrene (DTAS)

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.
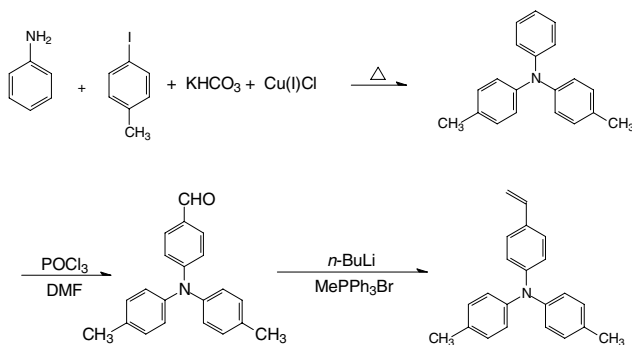
B. Synthesis and Characterization of Organic Transporting Copolymers
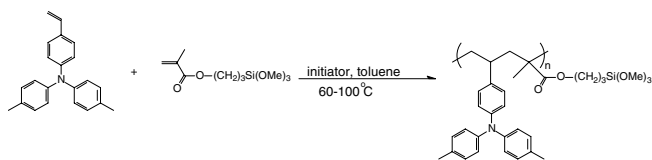
Under an Argon atmosphere, the silane and charge transporting monomer mixture with predetermined molar ratio was dissolved in anhydrous toluene. The radical initiator then added to the solution. After the solution was heated to 60 °C-100 °C for 20 hours, the contents were cooled to room temperature and precipitated into methanol. The polymer was collected by filtration, washed with hexane several times, and dried under vacuum overnight.

C. Sol-gel Solution Preparation

The sol-gel solutions were prepared by the acidic hydrolysis and condensation of the copolymers with methyltrimethoxysilane (MTMS) as shown.[9]
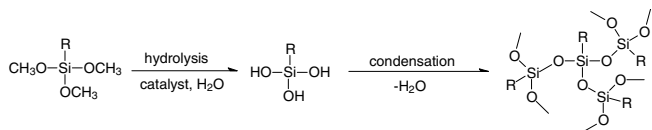
R represents either an alkyl group or an alkylene group from the repeat unit of the transporting copolymers.

For comparison, a sol-gel solution without transporting copolymer was prepared with only methyltrimethoxysilane.

D. 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.

E. Electrophotographic Characterizations

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}s, 775 nm).

Results and Discussion

The copolymers containing both silane and charge transport groups were synthesized through radical polymerization. A ^{1}H NMR spectrum of poly(DTAS-MATMS) is shown in Figure 1. There are no impurity peaks, such as those from residual monomers and solvents, in the spectrum. The relative ratio of the triphenyl amine 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.
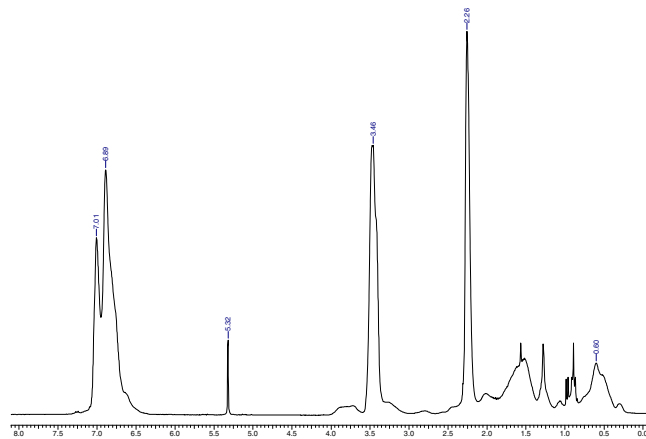

Figure 1. ^{1}H NMR spectrum of poly(DTAS-MATMS)

Table 1. Copolymerization of DTAS and MATMS.

#	feed ratio A/B* (mol %)	A/B* in polymer (mol %)	Tg (°C)	Mn	Mw	E$^0_{ox}$ (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

*: Monomer A: DTAS; Monomer B: MATMS

The copolymerization results of poly(DTAS-MATMS) with different comonomer ratios are shown in Table 1. 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 2 lists the photoreceptors, the sol-gel characteristics, and the residual potential. With either substrate the higher the content of charge transporting monomer in the sol-gel coating the lower the residual potential (V_{res}).

Table 2. photoreceptor films from sol-gel process and the sensitometric properties.

sample	substrate	CTM	CTM / MTMS Ratio (wt)	CTM % in sol-gel (wt %)	sol-gel thickness (μm)	V_{res} (V)
Control **1***	A	N/A	N/A	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	**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	**P4**	3:1	48.1	1.8	1

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

As shown, photoreceptors with sol-gel coats of copolymer **P4** on CTL or CGL substrates exhibited almost 100% photodischarge relative to the photoreceptor of Control **1** (no overcoat) and a sol-gel overcoat with only MTMS but no charge transport material (Control **3**) exhibited no photodischarge.

Conclusion

This study has demonstrated that the copolymerization of charge transport and silane monomers and the incorporation of this copolymer into a 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.

Acknowledgement

References

1. M. Kumakura, I. Kaetsu, M. Horigome, T. Isomura, T. Yoneyama, and T. Murata, US patent 4,912,000 (1990)
2. R. L. Schank and J. A. Bergfjord, US Patent 5,204,201 (1993)
3. L.-H. Lee, D. J. Nichol-Landry and C. J. Tarnawskyj, US patent 4,606,934 (1986)
4. R. L. Schank, US patent (1986)
5. C. J. Brinker and G. W. Scherer, *Sol-gel Science*; Academic Press: Boston, 1990.
6. R. H. Baney, H. Itoh, A. Sakakibara, and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995).
7. W. T. Ferrar, D. S. Weiss, J. R. Cowdery, and L. G. Parton, *J. Imaging Sci. Tech.*, **44**, 429 (2000).
8. D. S. Weiss, W. T. Ferrar, J. R. Corvan, L. G. Parton, and G. Miller, *J. Imaging Sci. Tech.*, **43**, 280 (1999).
9. D. S. Weiss, W. T. Ferrar, J. R. Cowdery-Corvan, J. A. Sinicropi, and M. B. O'Regan, US patent (1997)
10. W. T. Ferrar, J. R. Cowdery-Corvan, E. T. Miskinis, C. Newell, D. S. Rimai, L. J. Sorriero, J. A. Sinicropi, D. S. Weiss, and N. Zumbulyadis, US patent 5,874,018 (1999)
11. W. T. Ferrar, L. J. Sorriero, J.S. Cowdery, and D. S. Weiss, US patent 6,066,425 (2000)
12. T. Ikegami, Y. Suzuki, H. Nakai, N. Tamoto, and K. Kishida, US patent 6,030,736 (2000)
13. H. Kobayashi and N. Kushibiki, US patent 5,712,360 (1998)
14. N. Kushibiki and K. Takeuchi, US patent 5,688,961 (1997)
15. N. Kushibiki and K. Takeuchi, US patent 5,824,443 (1998)
16. W. Yamada, K. Nukada, and M. Iwasaki, US patent 6,046,348 (2000)
17. E. Bellmann, G. E. Jabbour, R. H. Grubbs, and N. Peyghambarian, N. *Chem. Mater.*, **12**, 1349 (2000).
18. M. Schneider and K. Mullen, *Chem. Mater.*, **12**, 352 (2000).
19. F. Ribot, and C. Sanchez, *Comm. on Inorg. Chem.*, **20**, 327 (1999).
20. C. Sanchez, F. Ribot, and B. Debeau, J. *Mater. Chem*, **9**, 35 (1999).
21. C. Sanchez and F. Ribot, *New J. Chem.*, **18**, 1007 (1994).
22. T. Suratwala, *Chem. Mater.*, **10**, 199 (1998).

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.