Flexographic Printing with Conductive Colloidal Inks Composed of Polyaniline Coated Poly(butyl methacrylate) Particles.

Moon Gyu Han[a], Jay Sperry[b], Amit Gupta[b], Christopher F. Huebner[a],
Samuel T. Ingram[b], and Stephen H. Foulger[a,*]

Center for Optical Materials Science and Engineering Technologies
[a]School of Materials Science and Engineering
[b]Department of Graphic Communications
Clemson University, Clemson, SC 29634-0971, USA

[*]To whom correspondence should be addressed; e-mail: foulger@clemson.edu.

September 15, 2006

In the last two decades since the demonstration of the first organic field-effect transistor (OFET), researchers have been expanding the knowledge in this field over a range of areas, including materials development, device design, modeling, and deposition processes[1]. Organic and all-polymer transistor circuits with performance characteristics suitable for limited applications have already been demonstrated, though the expansion of organic electronics into a range of applications has been suggested, for example, radio frequency identification tags, sensors, and simple & rugged displays, to name a few. The inherent advantage in organic/polymeric systems, relative to inorganic systems that are fabricated through established lithography routes, is the potential that low-cost, large area electronics may be realized when these materials are coupled with conventional ink-jet[2], screen[3], or roll-to-roll[4-6] printing technologies.

The majority of efforts to couple device-suitable polymeric systems with roll-to-roll printing methods have focused on commercially available polymeric solutions or dispersions[5, 6]. These systems have established that roll-to-roll printing methods are a potential route for large-scale organic device fabrication and have provided insights into the relationship between the specialized inks, their printability, and the final device performance. A broader control over the properties of the inks utilized in large area printing of organic devices will be required as this field matures. Opportunities exist to establish a greater control on the properties of the ink through recent advances in the colloidal chemistry of intrinsically conductive polymers. To this end, we report on the utilization of polyaniline-poly(butyl methacrylate) core-shell particles for use as colloidal inks in flexographic printing. In general, the exploitation of a core-shell topology results in the appearance of particles that exhibit new properties[7].

Figure 1 presents a schematic of the flexographic printing press employed in this effort. In this printing technique, relief plates comprised of a flexible photopolymer are mounted on a plate cylinder. The flexographic plates were derived from a digital platemaking process that requires the laser ablation of an opaque carbon mask to create the image area and then a UV face exposure to harden the image area. The plates were then thermally processed creating a printing relief of 508 μm with image features down to 7.6 μm. The print image consists of a raised surface that is wetted with the conductive colloidal ink from the anilox inking rolls and then is pressed onto the substrate with the impression cylinder. This printing technique is capable of producing good quality impressions on many different substrates and is both a low-cost and simple printing process used for decorating and package printing. The flexographic printing process captures 20.4% of the

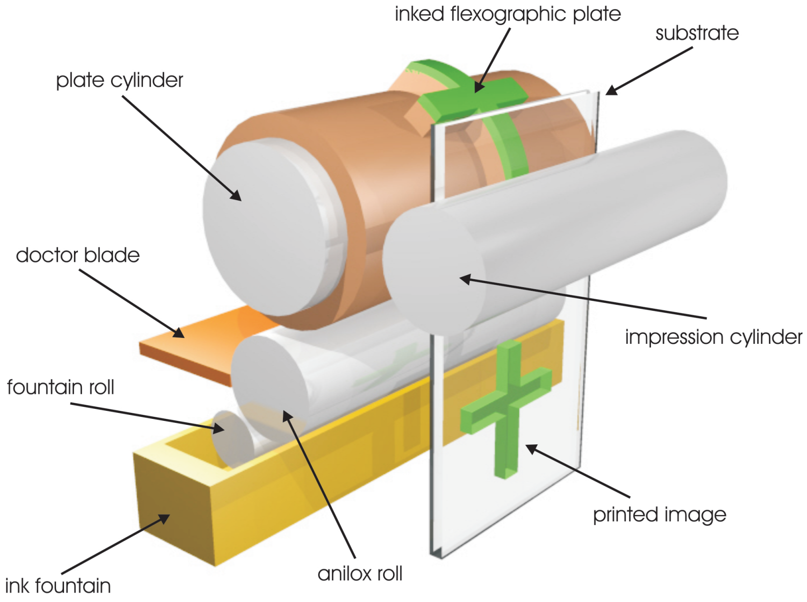

Figure 1: Schematic of the flexographic printing process.

global printing industry, resulting in approximately 121 billion dollars[8].

The conductive colloidal ink was composed of core-shell particles; Figure 2 presents a schematic of the procedure employed to synthesize the poly(butyl methacrylate) (PBMA) core particles and the corresponding polyaniline (PANI) shell around the PBMA spheres. The synthesis of the PBMA particles follows a typical emulsion polymerization and results in monodisperse ca. 200 nm diameter particles which exhibit a relatively low glass transition of 35 °C. These particles are then employed as the starting materials for the core-shell polymerization.

The particles are initially adsorbed with poly(N-vinylpyrrolidinone) (PVP) which acts to stabilize the particle at the low pH values that are experienced during the course of the shell synthesis, as well as serve as an anchor molecule between the PBMA core and the polymerizing aniline. The addition of aniline-HCl and ammonium peroxydisulfate (APS) initiates the polymerization of aniline onto the surface of the PBMA latex[9, 10]. The resulting green dispersion was cleaned through centrifugation, with the sediment being redispersed in isopropanol. To this dispersion several other

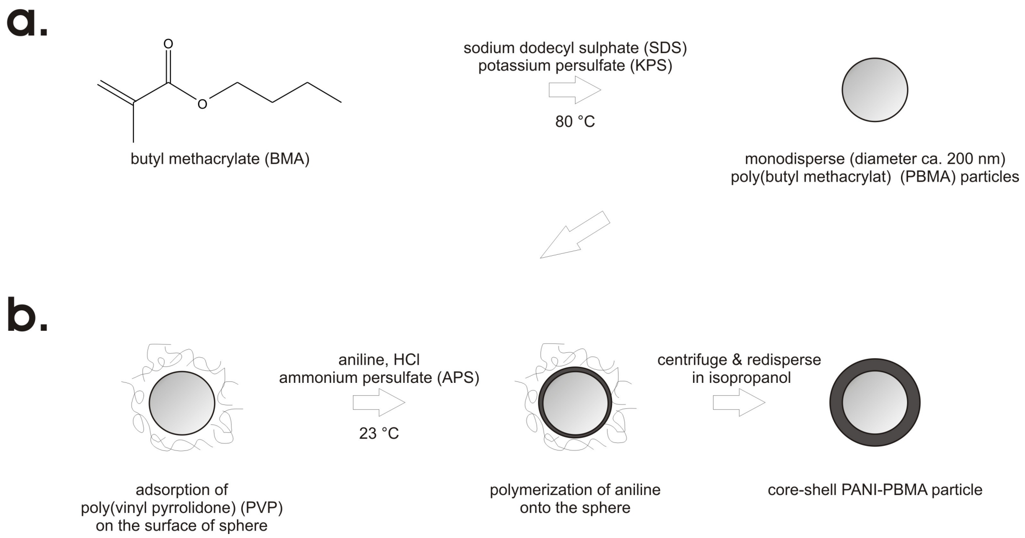

Figure 2: Procedure for synthesizing polyaniline-poly(butyl methacrylate) core-shell particles for use as colloidal inks in flexographic printing: **(a.)** aqueous emulsion polymerization of butyl methacrylate utilizing the surfactant sodium dodecyl sulfate and initiator potassium persulfate results in monodisperse particles with diameter of ca. 200 nm and a glass transition of ca. 35 °C and **(b.)** the poly(butyl methacrylate) spheres were coated with the polymeric stabilizer polyvinylpyrrolidone after which aniline-HCl was oxidatively polymerized with ammonium persulfate around the spheres.

components (cf. experimental section) were added to form the conductive colloidal ink. In general, flexographic inks are usually composed of colorants and liquid vehicles. The electrically conductive core-shell particles are the replacement of the colorant while isopropanol is used as the major solvent vehicle to endow the appropriate rheological, wetting, and drying properties of the ink for the flexographic process.

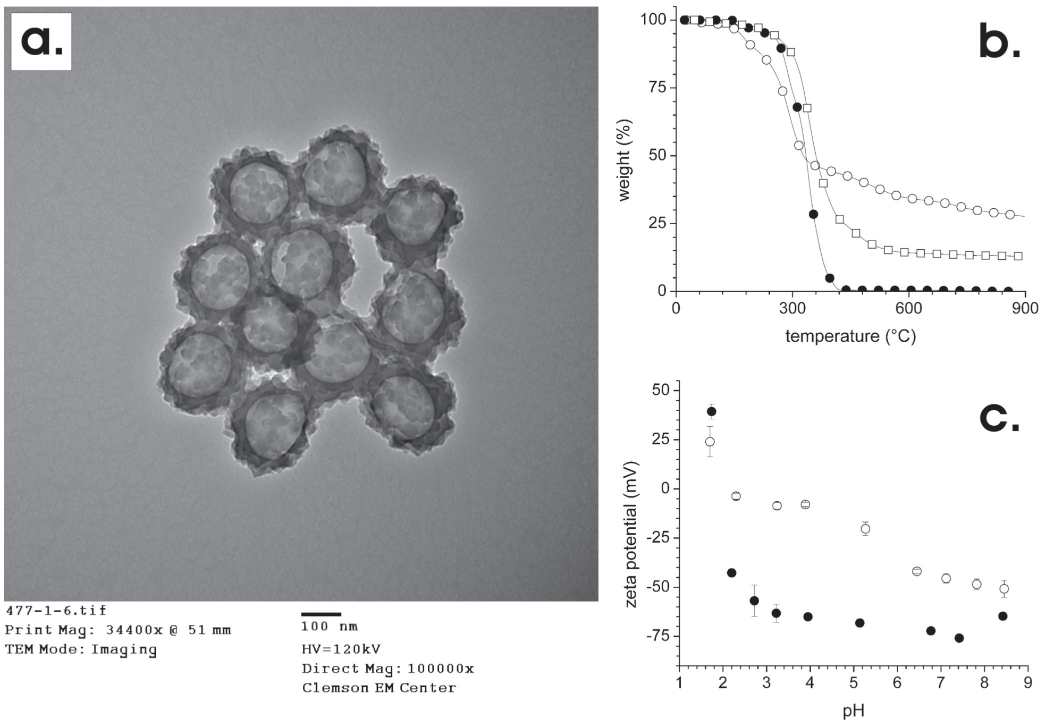

Figure 3: **(a.)** Transmission electron micrograph of polyaniline coated poly(butyl methacrylate) particles; **(b.)** themogravimetric analysis of polyaniline particles (○), poly(butyl methacrylate) particles (●), and polyaniline coated poly(butyl methacrylate) particles (□); **(c.)** zeta-potential of initial colloidal poly(butyl methacrylate) particles (●) and polyaniline-coated poly(butyl methacrylate) particles (○). Error bars represent standard deviation of mean value.

Figure 3a presents a TEM micrograph of the PANI-coated PBMA particles. The PBMA-core particles are ca. 200 nm in diameter and the PANI-shell is ca. 45 nm in thickness. The PANI completely covers the entire surface of the cores. One advantage for the use of a core-shell morphology is a reduction in material costs. By localizing the conductive region of the particles to the outer periphery prevents the waste of material in the core region which would normally be underutilized in a conductive network. Though PANI is relatively inexpensive, more expensive or exotic materials, such as poly(3,4-ethylenedioxythiophene), could be utilized in this topology[11]. An additional advantage of the core-shell topology is the elimination of a binder material in the formulation of the inks, which can act to reduce the conductivity of a printed zone. The low glass transition of the PBMA core is expected to soften and deform during the printing process, resulting in a cohesion between adjacent colloidal particles without incurring a severe penalty in the measured electrical conductivity.

Figure 3b presents the thermogravimetric analysis of the coated particles, as well as the pure PANI particles and the pure PBMA particles. The pure PBMA particles decompose at an onset temperature of ca. 275 °C, and are completely volatilized by 450 °C. The pure PANI particles have a lower onset temperature for decomposition of ca. 150 °C, indicative of the early volatilization of dopant. The highly conjugated structure of the PANI results in the carbonization of the polymer with heating, producing a large quantity of char at 900 °C. The PANI-coated PBMA particles exhibit an onset to decomposition temperature that is slightly higher than the pure PBMA. The influence of the PANI shell is evident with the almost 13 w/w of char remaining at 900 °C in the PANI-PBMA core-shell particles. The observed content of PANI in the core-shell particles was 49.3 w/w.

Figure 3c presents the zeta-potential of the initial and PANI-coated particles over a range of pH values. The zeta-potential is defined as the electric potential at the imaginary shear plane separating the thin layer of liquid bound to the solid surface of the particles which exhibits elastic-like behavior and the rest of the liquid which exhibits normal viscous behavior. A general rule is that a colloid is stable due to the mutual electrostatic repulsion of the particles when the absolute value of the zeta potential is greater than 30 mV [12]. The initial uncoated PBMA particles exhibit

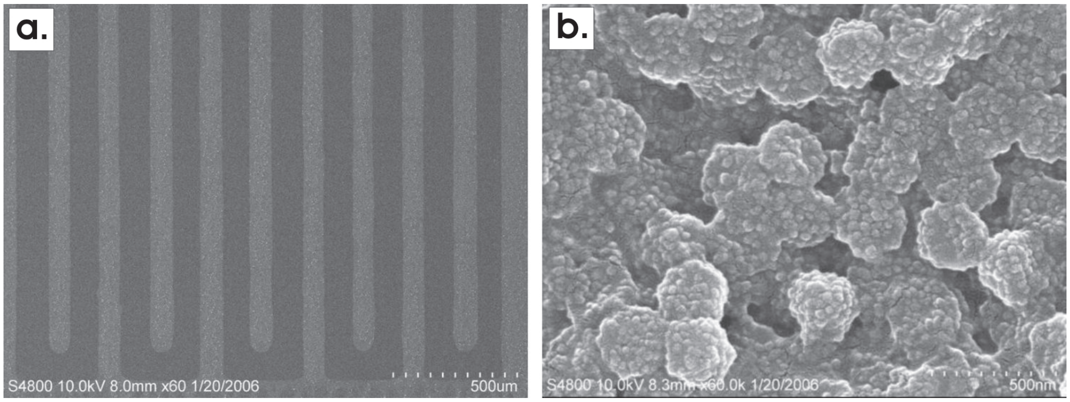

Figure 4: Scanning electron micrograph of: (**a.**) interdigital test figure flexographically printed with conductive ink composed of polyaniline-poly(butyl methacrylate) core-shell particles and (**b.**) morphology of the core-shell particles within a printed zone.

a high level of stability at the pH values between 3 to 9, with the zeta-potentials in this range of pH falling under -50 mV. The addition of the PANI shell to the particles moderately decreases their stability (cf. Figure 3c) as suggested by the drop in the absolute value of the zeta-potential of the coated particles. The coated particles exhibit zeta-potentials falling between -8 mV and -50 mV in the pH range of 3 to 9, with relatively stable particles at pH values greater than 5.

Figure 4a presents a scanning electron micrograph of a selected interdigital test figure flexographically printed with the conductive ink composed of PANI-coated PBMA particles. The printed test figure exhibited a line width that was ca. 85 μm, while the spacing between the lines was ca. 115 μm. The target design of the test figure was a line width of 50.8 μm and a spacing of 152.4 μm. The thickness of the printed zone ranged from 0.6 μm to 2.0 μm and was defined by the cell volume of the anilox roll as well as the viscosity of the ink. The difference in line widths and spacing stem from the spreading of the ink during the printing process and can be modified through a range of ink and process parameters. A number of test figures were reliably printed down to a line thickness of ca. 50 μm. The printed zone exhibits a volume resistivity of ca. 2 Ω·cm, though this conductivity could be modified by altering the composition of the ink. Figure 5 presents the electrical percolation characteristics of the PANI-PBMA core-shell particles diluted with pure PBMA particles. The volume resistivity of the printed section can vary as the polyaniline content is decreased in the ink from that of the pure PANI-coated PBMA particles to that of a PBMA-rich composition, though the change in volume resistivity with composition does not exhibit a simple linear additive characteristic. A printed zone composed only of the core-shell particles (cf. Figure 4) has a polyaniline content of 49.3 w/w and exhibits a volume resistivity of ca. 2 Ω·cm. Uncoated poly(butyl methacrylate) particles are electrically insulating and their addition to the core-shell ink results in an increase of the volume resistivity of a printed zone through a reduction in the conductive paths accessible to mobile charge. Significantly decreasing the polyaniline content in the ink to 19.6 w/w results in a printed zone with a volume resistivity of ca. 45 Ω·cm, a modest ca. 20 times increase from the "pure" core-shell ink. A further reduction of polyaniline in the ink to 9.8 w/w results in the printed zone exhibiting an abrupt increase in volume resistivity to $1.0\mathrm{x}10^4$ Ω·cm. With 9.8 w/w of polyaniline in the ink, the percolation threshold of the composition has been traversed and the volume fraction of the PANI becomes insufficient to provide continuous electrical paths through the bulk material[13]. Assuming the density of polyaniline to be 1.32 g/cm^3[14] and PBMA to be 1.05 g/cm^3[15], fitting the scaling relation $\sigma \propto (p - p_c)^t$ to the conductivity data, where p_c represents the volume fraction of the PANI-coated PBMA particles at the percolation threshold and the critical exponent t governs the scaling behavior in the region of p_c, results in a percolation threshold of ca. 7 v/v and a critical exponent of 2.4.

The conductivity of the test figure can also be influenced by the morphology of the particles. Figure 4b presents the morphology within a printed zone. In this type of quick contact printing, the particles do not have sufficient time to pack with any regularity and the printed zone has a significant level of "porosity". Since the measured volume resistivity of the printed zone is increased by regions that do not contribute to charge transfer, enhancing the printing pressure results in a

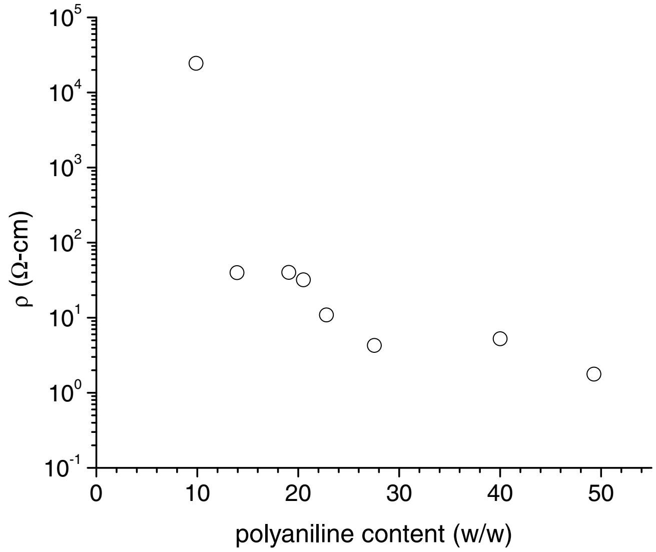

Figure 5: Volume resistivity of printed ink composed of polyaniline-coated poly(butyl methacrylate) particles mixed with neat poly(butyl methacrylate) particles.

more compact particle packing, raising the conductive cross section.

On valuable feature of the core-shell construction is the ability to decouple the conductive requirement (shell) from the thermomechanical properties (core) of the final particle. Figure 6 presents both the SEM micrograph of a printed zone after heat treating and the thermophysical properties of the particles. The glass transition of the PBMA cores is ca. 35 °C (cf. Figure 6b) and is clearly discernable in the differential scanning calorimetry trace of the PANI-coated PBMA particles. In Figure 6a, heat treating the printed zone for 3 hours at 60 °C results in a change in the morphology of the printed zone. The heat treatment has allowed the polymer particles to adjust their geometric characteristics from the initial spherical shape (cf. Figure 4b) to an almost planar structure (cf. Figure 6a). Due to the low electron contrast between the core and shell material, it is unclear if the particles have deformed but maintained their structural integrity or split open, releasing the PBMA core. Nonetheless, the heat treated printed zones exhibited higher levels of resistance to mechanical abrasion, indicating that the PBMA may be acting as a binder. Surprisingly, the measured conductivity of the heat treated and untreated samples were not significantly different.

The effect of the thermal treatment on the conductivity was further investigated. Figure 6c presents the conductivity ratio ($\sigma/\sigma_{25^{\circ}C}$) of a printed zone after being compressed at elevated temperatures under a pressure of 10 kpsi for 2 seconds. The conductivity of the printed zone was then measured at 25 °C and normalized relative to the initial value. Heating and compressing the printed zone resulted in a decrease in the room temperature conductivity. The drop in measured conductivity was enhanced as the thermal treatment was performed at temperatures that progressively deviated from the glass transition of the PBMA. It is speculated that the viscosity of the PBMA was reduced with the elevated temperatures and during the short compression time, a higher level of flow occurred and assisted in disrupting the conductive network of the polyaniline shell, resulting in the decrease in measured conductivities.

In summary, we believe the effort described here is the first example of utilizing intrinsically conductive polymer core-shell particles for use as conductive colloidal inks in flexographic printing. The ability to tune the conductivity of the ink prior to printing through the colloidal composition as well as after printing with a thermal treatment may be a valuable resource for future designers of organic devices.

Experimental Section

Synthesis of particles. The initial phase of the core-shell synthesis was the emulsion polymerization of poly(butyl methacrylate) particles with a particle size between 100 nm - 300 nm. In a typical synthesis run, 0.4 g of sodium dodecyl sulfate (SDS) was added to 320 g of deionized water into a reaction vessel equipped with stirrer and a N_2 purge. After stirring for 1 hour, 160 g of butyl methacrylate monomer was injected into the vessel and the reaction was heated to 80 °C. The polymerization was initiated by the addition of 0.33 g of potassium persulfate (KPS) which

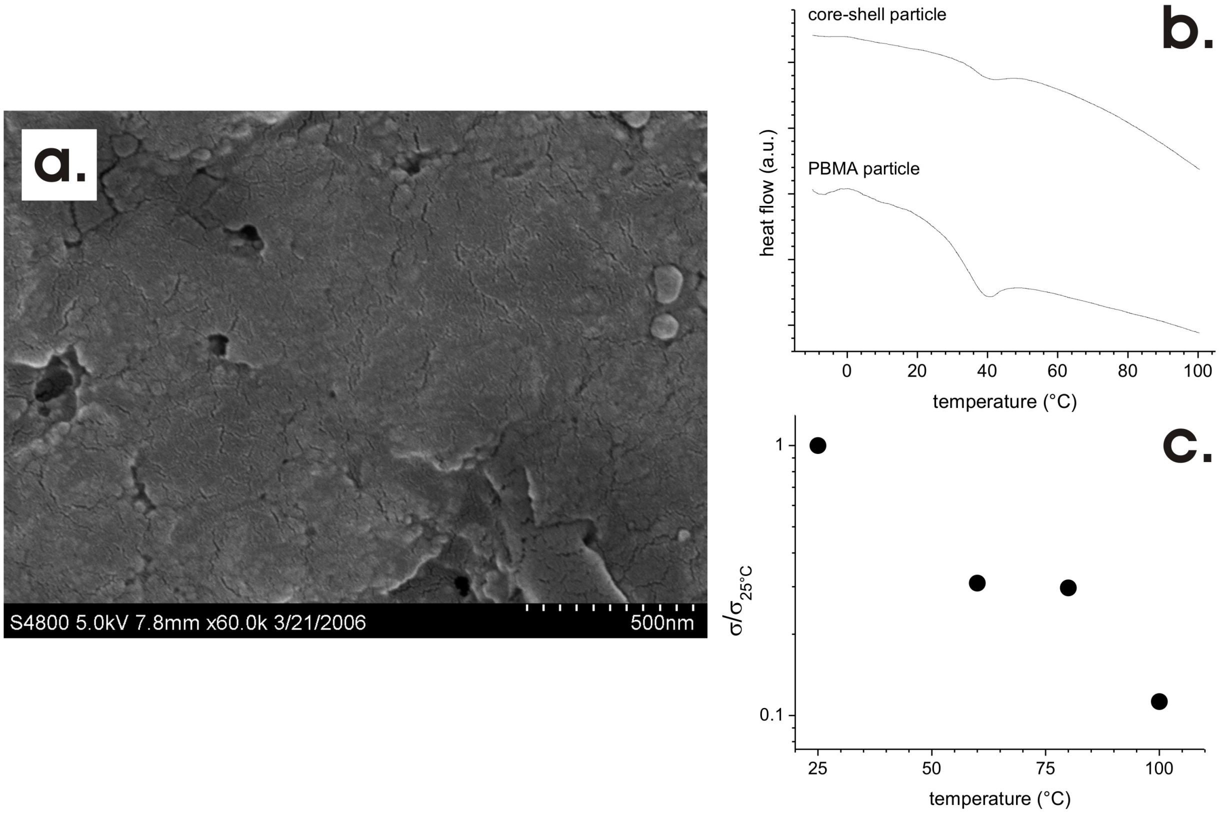

Figure 6: (**a.**) Scanning electron micrograph of a printed zone after being thermally treated for 3 hours at 60 °C (compare to Figure 4b); (**b.**) differential scanning calorimetry traces of the neat poly(butyl methacrylate) and polyaniline-coated poly(butyl methacrylate) particles, indicating a glass transition temperature of ca. 36 °C; and (**c.**) conductivity ratio of printed zones after being heated and compressed at 10 kpsi for 2 seconds (conductivity measured at 25 °C and normalized relative to initial value).

was dissolved in 10 g of deionized water. The polymerization was allowed to proceed for 6 hours before cooling to room temperature. The observed particle diameter from transmission electron microscopy (TEM) was 199±4 nm. The observed Mw of the colloidal particles was 221k and the polydisperse index (PDI) was 2.08.

The second step in the core-shell synthesis is to coat the PBMA particles with polyaniline. To protect the PBMA particles from flocculation in the low pH synthetic conditions, poly (N-vinylpyrrolidinone) (PVP), a polymeric stabilizer, was dissolved into the suspension and allowed to absorb onto the particles. In 400 ml of the latex dispersion, 400 ml of deionized water was added to dilute the dispersion and then a PVP solution (40 g of PVP / 400 ml water) was added. To this dispersion, 78 g of aniline-HCl was added to the reaction vessel. After the aniline-HCl was dissolved, 124 g of ammonium peroxydisulfate (APS) (initially dissolved in 400 ml water) was added to initiate the polymerization at room temperature. The reaction was allowed to proceed for 3 hours, after which the resulting core-shell particles were purified by centrifugation.

Formulation of the colloidal ink. To form the colloidal ink, the cleaned core-shell particles were re-dispersed in isopropanol (IPA) and stirred. IPA was employed as the majority solvent due to its ability to allow the ink to effectively wet and spread on the polyethylene terephthalate (PET) printing substrate. The majority solvent was IPA, but water was utilized as a cosolvent and plasticizer. In addition, glycerin was added to the ink to control the drying rate of the printed ink. The composition of the ink was: core-shell particles (26.5 w/w), IPA (60.5 w/w), water (10 w/w), and glycerin (2 w/w).

Printing procedure. Print runs were done on Comco International Captain 6 station 10 inch narrow web inline press. A digitally imaged DuPont DFH plate with a caliper of 0.17 cm was thermally developed using a DuPont FAST processor. The test image was an interdigital template with various line widths, ranging from 25.4, 50.8, 254 and 512 μm, and spaces, ranging from 152.4, 203.2, 254, 304.8, 355.6, 406.4, 457.2, and 508 μm. Plates were mounted on Mark Andy manual plate mounter using 3M EH1715 cushion mounting material. Drying is a major consideration for flexography, so the inline infrared drying station, measuring 61 cm in length and containing six 700 hundred watt bulbs, was maintained at 80 °C during the runs.

A modified ink pan was used for this study that required ca. 700 ml of the conductive ink. A banded anilox roll was employed which had five bands 1.75 in wide with varying cell depths and line rulings. The bands measured 0.95, 1.58, 2.1, 2.61, 3.01 bcm/ sq. inch. The substrate was a 0.25 mm thick PET sheet and was printed at 15.25 m/min.

Characterization. The zeta potential of the particles were measured over a range of pH values with a ZetaPlus zeta potential analyzer (Brookhaven Instruments Corp.).

A differential scanning calorimeter (TA Instruments DSC 2920) equipped with liquid nitrogen cooling accessories was employed for identifying T_g. The carrier gas was nitrogen at a flow rate of ca. 60 mL/min. Scans were made from -30 °C to 100 °C at a scanning rate of 10 °C/min. Thermal gravimetric analysis (TA Instruments TGA 2950) was carried out under a nitrogen purge from 20 °C to 900 °C at a rate of 20 °C/min. Molecular weights of the PBMA colloid were determined by GPC (THF at 1.0 ml/min) in 1 mg/mL solution in THF, using a Waters 515 pump, four 7.8x300 mm Styragel columns (HR- 2, 3, 4, 6) and a Waters 2414 refractive index detector. Reported molecular weights are relative to narrow distribution polystyrene standards (Mw = 2330 - 980,000).

For electron microscopy imaging, the coated particles were dropped on Formvar carbon stabilized copper grids (Ted Pella Inc. 01753-FX1) and dried at room temperature under a watch glass.

The samples were imaged using a Hitachi H-7600 transmission electron microscope (TEM) at an accelerating voltage of 120 kV and 10 μA. Scanning electron microscopy was done with a Hitachi S-4800 Field Effect Scanning Electron Microscope (FE-SEM) at a working voltage of 5-10 kV.

The volume resistivity of the printed zone was measured with an Alessi C4S four-point head mounted on an Alessi CPS-05 contact probe station. Current was supplied to the head with a Keithley 220 programmable current source and voltage drop across the samples was measured with a Kiethley 2000 digital multimeter. The applied current ranged from 1 to 4 μA.

All data taken at a temperature of 23 °C unless otherwise noted.

1 Acknowledgements.

The authors thank DARPA (Grant Number: N66001-04-1-8933) and the National Science Foundation through a CAREER award (Grant No. DMR-0236692) (SHF) for financial support.

References

[1] T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel, and S. D. Theiss. *Chem. Mater.*, 16:4413, 2004.

[2] T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, and J. C. Sturm. *Appl. Phys. Lett.*, 72:519, 1998.

[3] F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava. *Science*, 265:741, 1994.

[4] M. Pudas, N. Halonen, P. Granat, and J. Vähäkangas. *Progress in Organic Coatings*, 54:310, 2005.

[5] J. A. Rogers, Z. Bao, A. Makhija, and P. Braun. *Adv. Mater.*, 11:741, 1999.

[6] T. Mäkelä, S. Jussila, H. Kosonen, T. G. Bäcklund, H. G. O. Sandberg, and H. Stubb. *Synth. Met.*, 153:285, 2005.

[7] W. Schärtl. *Adv. Mater.*, 12:1899, 2000.

[8] Pira International Ltd. The Future of Global Printing Strategic Quantitative Forecasts and Expert Insight.

[9] D. B. Cairns, M. A. Khan, C. Perruchot, A. Riede, and S. P. Armes. *Chem. Mater.*, 15:233, 2003.

[10] J. Stejskal, P. Kratochvíl, S. P. Armes, S. F. Lascelles, A. Riede, M. Helmstedt, J. Prokeš, and I. Křivka. *Macromolecules*, 29:6814, 1996.

[11] M. G. Han and S. H. Foulger. *Adv. Mater.*, 16:231, 2004.

[12] R. M. Fitch. *Polymer Colloids: A Comprehensive Introduction.* Academic Press, New York, 1997.

[13] F. Lux. *J. Mater. Sci.*, 28:285, 1993.

[14] J. Stejskal and R. G. Gilbert. *Pure Appl. Chem.*, 74:857, 2002.

[15] C. Zhou, Y. Zhao, T-C Jao, C. Wu, and M. A. Winnik. *J. Phys. Chem. B*, 106:9514, 2002.