ACS APPLIED MATERIALS & INTERFACES

Design of Colored Multilayered Electrophoretic Particles for Electronic Inks

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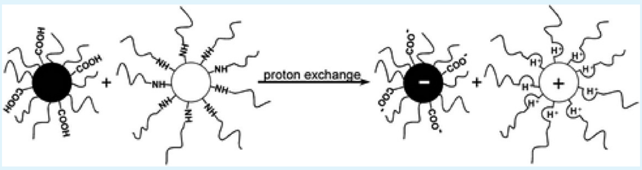


ABSTRACT: The preparation of multilayered latex particles with surface functional groups suitable for use as electrophoretic particles in electronic inks has been studied. The particles are formed by dispersion polymerization and have a polystyrene core, slightly cross-linked with divinylbenzene (DVB), and a poly(methyl methacrylate) (PMMA) or a poly(acrylic acid) (PAA) shell. After grafting alkyl chains on their surface, the particles are negatively or positively charged and sterically stabilized against aggregation in nonpolar solvent. The particles were dyed by incorporation of Nigrosin during polymerization or by swelling in supercritical CO_2 in the presence of a dye. Particle size, morphology, incorporated dye content and zeta potential were determined. A dual-particle electronic ink based on a mixture of the colored multilayered particles and white hybrid TiO_2-polymer particles was prepared and electro-optically tested.

KEYWORDS: electrophoretic particles, dispersion polymerization, colored particles, supercritical CO_2 dyeing

INTRODUCTION

Electrophoretic image displays (EPID) have been the subject of intense research and development for a number of years.[1−4] The large interest in such a display is based on its many advantages: low power consumption, low cost, wide viewing angles, image memory, lightweight, flexibility. The dual-particle EPID consists in a suspension of two kinds of colored and oppositely charged particles in a dielectric medium, the electrophoretic ink, sandwiched between two flexible electrodes. Under the influence of an electric field, the particles migrate toward the electrode of opposite charge. The front electrode (the viewing electrode) is transparent, whereas the back electrode is used for pixel addressing. Each pixel takes the color of the particles that have migrated to the front.

The optical and electrical properties of an EPID depend on the composition of the electrophoretic ink. The particles synthesized must have relatively small sizes, between 500 and 1500 nm, and should contain a reasonable amount of dye or colored pigments. Moreover the particles must be charged. Hsu et al.[5] have shown that particles can be charged in nonpolar media if their counterions are separated and stabilized in charged inverse micelles. Therefore, in most of the electrophoretic inks a charging agent or a surfactant is included that forms inverse micelles capable of stabilizing the counterions. However, the presence of these micelles presents also important drawbacks since their migration into the device is responsible for hydrodynamic instabilities,[6] electric field screening,[7] and electric current generation.[8]

We present here the synthesis of particles for use in dual particle electrophoretic ink without surfactant. For this purpose, acidic and basic particles of contrasting colors are synthesized, the mixing of which will lead to spontaneous transfer of a proton from the acid to the base, with no need of micelles to stabilize counterions (Scheme 1). Particle countercharging will thus result in improved lifetimes of the display and reduced power consumption. Finally, such particles must be sterically stabilized by long alkyl chains grafted on their surface that prevent aggregation of oppositely charged particles.

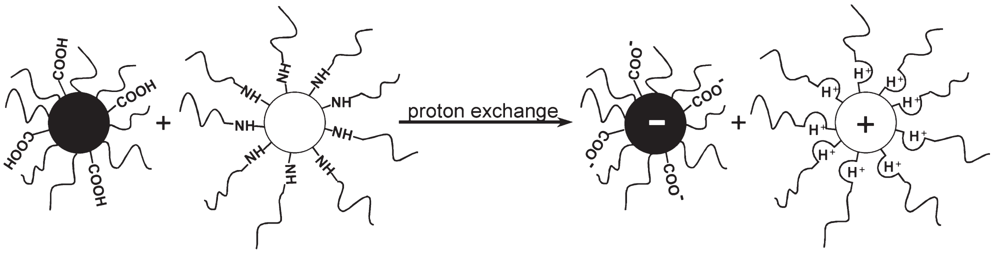
The synthesis and characterization of functionalized latex particles having specific properties has been an active area in both academia and industry. To synthesize such particles, various heterogeneous polymerization techniques can be used.[9−11] Among them, dispersion polymerization is a very versatile method as it allows for the use of a large variety of monomers and comonomers. The monomers are soluble in the continuous phase, whereas the resulting polymer is in poor solvent. Phase separation occurs during polymerization, in the presence of a polymeric stabilizer, resulting in monodisperse polymer particles with sizes ranging from 100 nm to 10 μm.[12,13] Moreover this technique allows for easy functionalization of the particles, by introduction of a second monomer and initiator in a second step.

Recently, colored particles have been obtained by pigment encapsulation.[14−19] A dye can also be encapsulated during polymerization[20,21] or after particle formation.[22,23]

Received: June 24, 2011
Accepted: August 24, 2011
Published: August 25, 2011

dx.doi.org/10.1021/am200815a | *ACS Appl. Mater. Interfaces* 2011, 3, 3602–3610

Scheme 1. Countercharging of Functionalized Particles in the Electrophoretic Dispersion Medium



In this paper we present the preparation of sterically stabilized electrophoretic particles incorporating dyes, by dispersion polymerization, for use in a dual-particle electrophoretic system.

The particle coloration is achieved via two different methods: dyeing by polymer particle swelling using the versatile method of supercritical CO_2[23] and polymerization in the presence of black dye Nigrosin, in a single-step process.

The colored particles obtained have been tested in a dual-particle electrophoretic ink (Scheme 1), containing white TiO_2/polymer particles as the second type of particles.

EXPERIMENTAL SECTION

Materials. Marcol 52 paraffin oil was obtained from ESSO. OLOA 1200 (polyisobutylene succinimide) was offered by Chevron Texaco and TiO_2 (rutile, RL-11A) was obtained from Millenium Chemicals. Kraton L-1203 (hydroxyl terminated ethylene-butylene copolymer), M_n = 7600 g mol^{-1} was offered by Shell Chemicals and was dried before use. Sudan Red 7B was purchased from Acros, Solvent Blue 35, Sudan Black B, Oil Blue N, dicyclohexylcarbodiimide (DCC), Nigrosin, dimethylaminopyridine (DMAP), 2,2′-azobis-(isobutyronitrile) (AIBN), polyvinylpyrrolidone(PVP), were obtained from Aldrich. Styrene, methyl methacrylate, and divinylbenzene were passed through a column of basic Aluminum oxide before use to remove the inhibitor. Dimethylformamide (DMF) was dried on molecular sieves and acrylic acid was distilled under reduced pressure before use. All monomers were stored in the fridge to avoid unwanted reactions.

Synthesis of PS/DVB Microparticles (1) via Dispersion Polymerization. In a three-necked 250 mL flask, equipped with a mechanical Teflon stirrer and nitrogen inlet, PVP (1 g) was dispersed in EtOH (120 mL). After bubbling nitrogen through the medium for 10 min, the reaction mixture was heated to 70 °C and styrene (10 mL), a corresponding amount of divinylbenzene (1 mL) and AIBN (0.5 g) were added. The reaction was stirred at 500 rpm. After 12 h, the reaction mixture was centrifuged (4000 rpm, 15 min) and the precipitate was washed with EtOH three times, followed by dialysis against water to remove excess of surfactant. The product was dried overnight under vacuum yielding a white powder with a monomer conversion higher than 95%.

Synthesis of PS/DVB-PAA Microparticles (2) and PS/DVB-PMMA Microparticles (3) via Dispersion Polymerization. In a three-necked 250 mL flask, equipped with a mechanical Teflon stirrer and nitrogen inlet, PVP (1 g) was dispersed in EtOH (120 mL). After bubbling nitrogen through the medium for 10 min, the reaction mixture was heated to 70 °C and styrene (10 mL), a corresponding amount of divinylbenzene (1 mL) and AIBN (0.5 g) were added. The reaction was stirred at 500 rpm. After 8 h acrylic acid (0.5 mL), for the synthesis of (2), or methyl methacrylate (0.5 mL) for the synthesis of (3), were added with AIBN (0.25 mL). After 12 h, the reaction mixture was centrifuged (4000 rpm, 15 min) and the precipitate was washed with EtOH three times, followed by dialysis against water to remove excess of surfactant. The product was dried overnight under vacuum yielding a white powder with a monomer conversion higher than 95%.

Microparticles can be also synthesized via dispersion polymerization in presence of dye. In this case, a dye (2 g), for example Nigrosin, is added in the beginning with the styrene. The general process is still the same.

Particle Swelling in Supercritical CO_2. A 20 mL steel reactor with special sapphire viewing windows for reactions in the supercritical CO_2 was charged with previously synthesized dried PS/DVB microparticles (1 g), Sudan Black (0.2 g), and methanol (10 mL). The reactor was sealed and heated to 35 °C. CO_2 was allowed in the cell using a 260D ISCO syringe pump and the pressure was brought up to 150 bar. The reaction mixture was stirred using a cross-shaped magnetic stirrer. After 12 h, the reactor was cooled and the contents were vented out and collected. The particles were washed 10−15 times with portions of 200 mL of ethanol by repeated centrifugation/redispersion steps to remove the excess unincorporated dye. The clean product was dried overnight under vacuum, yielding a dark blue powder.

Amidation of Colored PS/DVB-PMMA Microparticles with OLOA 1200. In dry glassware, black PS/DVB-PMMA microparticles (2 g) were added to OLOA 1200 (2 g) in dry DMF (15 mL). The mixture was ultrasonicated for 1 h and then, heated at 140 °C for 1 h. The reaction mixture was allowed to cool to room temperature, 20 mL of MeOH was added, and the mixture obtained was centrifuged for 30 min at 10 000 rpm. The residue was washed/centrifuged 6 times with hexane for 15 min at 7500 rpm. The particles (4) obtained were dried overnight under vacuum.

Esterification of PS/DVB-PAA Microparticles with Kraton L-1203. In dry glassware, Kraton (2 g) was stirred in dry DMF (50 mL) at 100 °C, under N_2. DMAP (0.8 g) and DCC (1.2 g) were then added to the flask, followed by 2 g of previously synthesized dried acid functionalized PS/DVB-PAA particles. The reaction mixture was stirred at 100 °C, under N_2 for 24 h. It was then allowed to cool to room temperature, was transferred to centrifuge tubes and washed 1 time with DMF and 3 times with EtOH by centrifuging for 15 min at 7500 rpm, removing the supernatant and redispersing in fresh solvent. The particles obtained (5) were dried overnight under vacuum.

Particle Characterization. After synthesis, the particles were washed by centrifugation−redispersion cycles in order to remove extra surfactant, initiator fragments, unreacted monomer or unincorporated dye. The amount of dye incorporated was determined by UV/vis spectroscopy, by dissolving the dye-containing particles in chloroform. A calibration curve was traced using a series of solutions of known concentrations to determine the extinction coefficients of the dyes used. The absorbance at the absorption maxima was used to calculate the concentration of dye in the particles. Particle size and morphology of the latex particles was determined by scanning electron microscopy (Jeol 6700F) and the particle size confirmation and size distribution profiles was done by dynamic light scattering (DLS, Malvern Zetasizer 2000).

Zeta potential of the particles was measured in a 10^{-3} M NaCl solution with a Malvern Zetameter 2000 and the electrophoretic mobility was calculated using the Schmoluchowsky equation, $\mu = \varepsilon\zeta/\eta$, where μ is the particle mobility, ζ is the particle zeta potential, ε is the dielectric constant of the dispersing medium, and η is the viscosity of the dispersing medium.

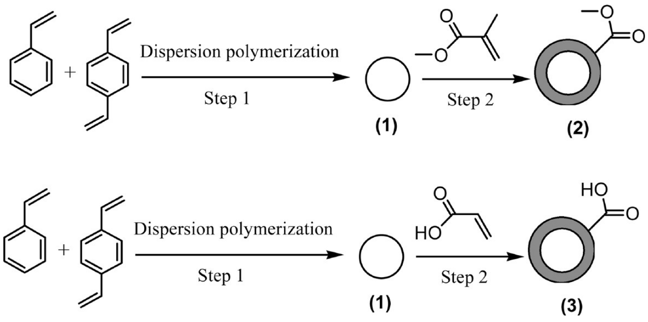
Electro-optical Devices. Electrophoretic dispersions are prepared by dispersing the synthesized particles in Marcol. The dispersion is then introduced in an electrophoretic cell, composed of two ITO-covered glass slides (2 × 3 cm) separated by a 50 μm thick Kapton spacer (optical area 15 × 15 mm). The cell is operated using a Keithley 230 programmable power source. For the determination of a time-resolved optical response the light scattering was measured under a 0° angle with a silicon photodiode. Illumination was under an angle of 30° with a 4 mW He/Ne laser (λ = 664 nm).[24] The contrast between white state and black state is defined as the ratio between the light scattering intensities of the white of the two states.[14,19] The residual current was measured with a programmable Keithley 6430 picoamperemeter.

RESULTS AND DISCUSSION

Synthesis of Multilayered Particles. The particles are cross-linked polystyrene beads obtained via dispersion polymerization in ethanol using PVP as stabilizer. The second monomer, methyl methacrylate, or acrylic acid is added in the second part of the polymerization in order to obtain either the ester or the acid functional groups on particle surface (Scheme 2) required for further particle functionalization by covalent grafting of different functional groups.

There are several factors that influence the polymer particle formation: stirring speed, nature of the monomer, its concentration relative to the aqueous phase, concentration and nature of surfactant, concentration and nature of initiator, and the difference in density and interfacial tension between the two phases.[25] These parameters have to be finely tuned for each polymerization system to obtain a good control of the process. Literature studies on the dispersion polymerization of styrene stabilized with polyvinylpyrrolidone (PVP) and cross-linked with divinylbenzene (DVB)[26] have shown that particle morphological deformations, incompatible with our application, can occur at particular cross-linker or stabilizer concentration and polarity of the polymerization medium.

Scheme 2. General Scheme of the Synthesis of PS/DVB-PMMA Particles (2) and PS/DVB-PAA Particles (3) via Successive Dispersion Polymerizations



Therefore, the dispersion polymerization of styrene cross-linked with DVB, initiated with AIBN, and stabilized with PVP was studied in preliminary experiments.

First we notice that the concentration of DVB cross-linker has no significant effect on particles size (entries A, C, E, and G). A slight increase in particle size and polydispersity are observed. A reason for this is that the cross-linked oligomers are formed in the dispersing medium and thus nuclei with larger size are produced, these nuclei growing into larger particles.[27] Furthermore, the range of DVB concentration is quite narrow, around 1.5%, for that reason it is difficult to observe a significant influence of this parameter. However, this value of cross-linker concentration allows us to have suitable particles for dye incorporation and the effect of its variation was not investigated anymore.

The amount of PVP stabilizer has a rather small effect on particles size. Particles size tends to decrease with PVP concentration (entries B and C or entries D, E, and F) especially for higher amounts (F), Similar effects of the PVP stabilizer upon the diameter of the formed polystyrene particles were reported in literature[27,28].

A slight increase in polarity was achieved by adding a small amount of water or by replacing the EtOH polymerization medium with MeOH. Particle size decreased and polydispersity increased with the increase in polarity of the polymerization medium, respectively pure ethanol, pure methanol and ethanol/water mixture (entries E, H, I). This observation can be explained by the difference in polarity between the medium and the monomer, as the monomer becomes less soluble in the dispersing medium with increasing medium polarity. In these conditions, the critical chain length for precipitated oligomers decreases and the rate of adsorption of the stabilizer increases. The rate of nuclei formation also increases, so the resulting particles are smaller.

Preparation of Colored Particles by Dyeing in Supercritical CO_2. Supercritical fluids easily diffuse into glassy polymers to produce a significant degree of swelling and plasticization that allows the mass transfer into polymer. Supercritical carbon

Table 1. Influence of Dispersion Polymerization Parameters on PS-DVB (1) particle size

	particle	polymerization medium	DVB (wt%)	PVP (wt%)	particle size* (nm)
A	PS	EtOH		3	990 ± 50
B	PS-DVB	EtOH	0.75	0.75	1700 ± 60
C	PS-DVB	EtOH	0.75	3	1300 ± 150
D	PS-DVB	EtOH	1.5	0.37	1590 ± 400
E	PS-DVB	EtOH	1.5	3	1980 ± 60
F	PS-DVB	EtOH	1.5	6	820 ± 260
G	PS-DVB	EtOH	4.15	3	1990 ± 80
H	PS-DVB	MeOH	1.5	3	1200 ± 310
I	PS-DVB	EtOH-H_2O(50%)	1.5	3	520 ± 680

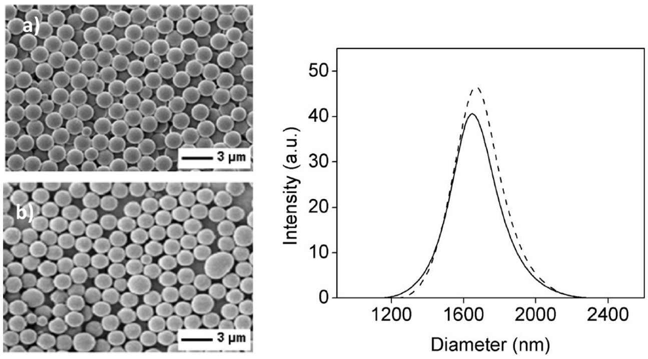
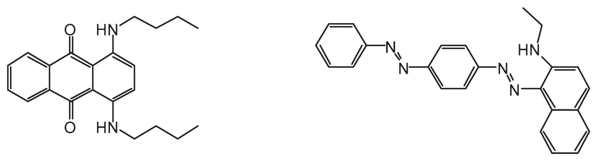
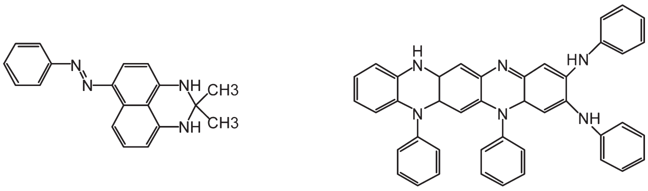


Figure 1. SEM micrographs and DLS particle size distribution profiles. (a) PS/DVB particles synthesized via dispersion polymerization (Table 1, entry B); DLS curve, plain line. (b) PS/DVB particles synthesized by dispersion polymerization (Table 1, entry B) after swelling in supercritical CO_2 in presence of Sudan Black; DLS curve, dashed line.

Scheme 3. Chemical Structures of Dyes Used in the Particle Supercritical CO_2 Dyeing



Solvent Blue 35 Sudan Red 7B



Sudan Black B Nigrosin

dioxide plasticizes polystyrene by reducing its glass-transition temperature,[29] polystyrene becoming a liquid at 30 °C and pressures above 100 bar. It has been shown that polystyrene particles could be swollen in supercritical CO_2[30] up to 1.8 times.

First, polystyrene particles were synthesized by dispersion polymerization in ethanol with 0.75% PVP and 0.75% DVB (Table 1, entry B). The particles were washed and dried as described in the Experimental Section and characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM), as shown in Figure 1. PS-DVB particles were then fed into the supercritical CO_2 reactor and were swelled in the presence of dyes, using heat and pressure. Different dyes were tested: Sudan Red, Sudan Black, Solvent Blue 35, Oil Blue N, and Nigrosin. (Scheme 3)

When CO_2 was added to the reactor containing the latex particles and the dye dissolved in methanol, the CO_2 phase appeared first transparent and distinct from the methanol phase. As pressure increased, under stirring, the two phases mixed, becoming one deep colored liquid phase. Methanol was expected to shift the partitioning of dye toward the polystyrene particles.

Table 2. Incorporation of Dye in Particles Swelled in Supercritical CO_2 after 12 h[a]

particle	dye	T (°C)	pressure (bar)	incorporated dye[b] (wt%)
PS/DVB	Sudan Red	35	250	0.56
PS/DVB	Sudan Black	35	120	0.61
PS/DVB	Sudan Black	35	150	0.77
PS/DVB	Sudan Black	35	250	0.72
PS/DVB	Solvent Blue 35	35	250	0.43
PS/DVB	Nigrosin	35	250	insignificant

[a] The PS particles are crosslinked with 0.7% DVB. [b] As determined by UV/vis spectroscopy.

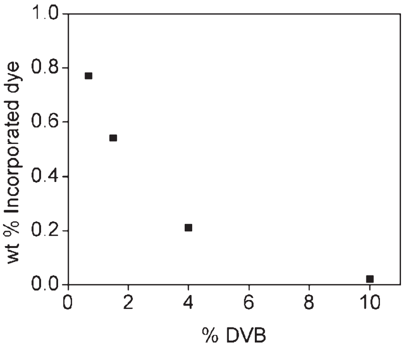


Figure 2. Influence of the degree of cross-linking (DVB) on the dye incorporation.

After 12 h, the particles were recovered as an intensely colored dispersion in methanol, by venting out the CO_2. Part of the colored particles in methanol were flushed out together with the CO_2, the rest were recovered by thoroughly rinsing the supercritical CO_2 reactor. The particles were then washed to remove the unincorporated dye by many stirring-centrifugation-redispersion washing steps with ethanol until the supernatant was colorless.

Particle size and morphology were not influenced by their swelling in supercritical CO_2, the resulting particles remaining nearly monodisperse, as shown in the scanning electron micrograph in Figure 1.

The amount of incorporated dye was determined by UV/vis spectroscopy (Table 2) after thoroughly washing off the excess unincorporated dye and particle drying under vacuum and is related to the nature of the dye and the supercritical CO_2 pressure used. Supercritical CO_2 dyeing results are presented in Table 2. Most of the dyes tested reached encapsulation up to 0.5 to 0.7%. The encapsulation of the much bulkier black dye Nigrosin was not successful, the PS/DVB particles remaining white upon supercritical CO_2 swelling with Nigrosin. A slight increase of encapsulated amount was observed for Sudan Black with increasing pressure from 120 to 250 bar. This is in accordance with the findings of Otake et al.[30] stating that the swelling degree of the particles increased with pressure. A reaction time of 6 h gave similar results as compared to 12 h reaction time.

Dyeing of the particles with Sudan Black was performed at various cross-linking degrees, at 250 bar. As depicted in Figure 2,

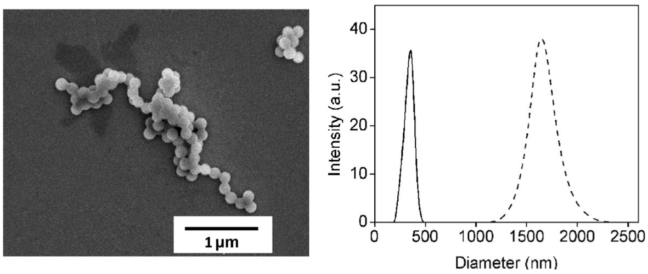


Figure 3. SEM micrograph (left) and DLS particle size distribution profiles (right) of PS/DVB particles obtained via dispersion polymerization (dashed line); and PS/DVB particles synthesized by dispersion polymerization in the presence of black dye Nigrosin (plain line).

Table 3. Dispersion Polymerization of Styrene/DVB in the Presence of Nigrosin

Nigrosin (wt %)	color	particle size* (nm)	yield (%)
	white	1700 ± 60	98
0.3	brownish	780 ± 40	95
0.75	black	620 ± 70	68
1.5	black	240 ± 55	65
2	black	240 ± 70	55

*Particle size as determined by DLS.

the amount of incorporated dye decreases with increasing cross-linking degree. The CO_2 swelled particles obtained were dark blue for 0.7% cross-linking and almost white at 10% cross-linking, maintaining at the same time their original shape and size upon swelling. Highly cross-linked particles could not be swollen by supercritical CO_2, and thus were not dyed. The dyeing of noncrosslinked particles was not possible either, SEM micrographs taken after dyeing showing particles that appeared crushed and disintegrated.

The results obtained are related to particle porosity, and particle cross-linking degree. The amount of DVB used for cross-linking in particle synthesis has to be low enough to allow particle plasticization and incorporate a sufficient amount of dye in supercritical CO_2. However, the particles must be mechanically strong in order to function within the electrophoretic dispersion during particle migration and switching between the two electrodes in the electrophoretic cell.

The PS/DVB particles dyed with Sudan Black in supercritical CO_2 required 10−15 stirring−centrifugation−redispersion washing steps and large quantities of washing solvent (ethanol) until a clear supernatant is left after the centrifugation of the dyed particles. After particle cleaning, there was no dye leaking out of the particles observed when the dyed particles were kept dispersed in ethanol.

Polymerization in the Presence of Dye. An alternative procedure to obtain highly cross-linked and colored particles in one preparation step is the polymerization in the presence of dye.

The dispersion polymerization of styrene cross-linked with divinylbenzene was studied in the presence of various organic dyes: Sudan Red, Solvent Blue 35, Oil Blue N, Sudan Black. The particles were formed in low conversions and did not incorporate the dye, even though attempts were made to shift the polarity of the continuous phase by adding water or by using methanol, to vary the ratio PS:DVB or the amount of AIBN used. Horack et al.[20] had already shown that dyes could interact and inhibit the polymerization reaction.

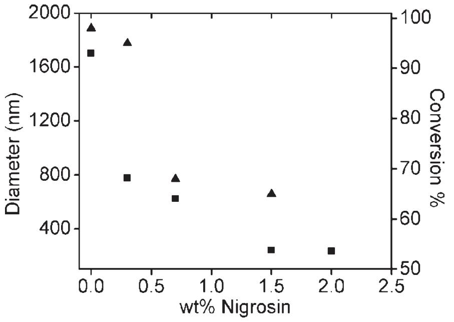


Figure 4. Particle size as a function of nigrosin wt% (■); conversion as a function of nigrosin wt% (▲).

However, the dispersion polymerization in presence of Nigrosin resulted in black particles and the process is only partly inhibited by the presence of dye. Nigrosin is completely miscible with styrene/divinylbenzene, but has a lower solubility in solvents such as ethanol or methanol. In Figure 3, SEM photographs and DLS particles size distribution of particles obtained by dispersion polymerization in the presence of black dye Nigrosin are shown.

In the dispersion polymerization process, the monomer polymerizes in the continuous phase, and the particle is formed by precipitation. The incorporation of dye into the particle depends on the diffusion of the dye molecules into polymer particle and their ability to precipitate with the polymer. In both cases it depends on the affinity of the dye toward the polymer. Results from the dye incorporation polymerization experiments are summarized in Table 3 and Figure 4.

Conversion and particle size decrease with increasing Nigrosin concentration. The presence of Nigrosin inhibited the radical polymerization and resulted in lower yields. However, black PS/DVB particles suitable for our application can be obtained with a rather narrow size distribution with a Nigrosin concentration around 0.75 − 1%.

Moreover, the PS/DVB particles obtained by dispersion polymerization in presence of Nigrosin required only 3−4 stirring-centrifugation-redispersion washing steps until the obtained particles would leave a clear supernatant after centrifugation. Compared to the supercritical CO_2 method the difference resides in the more intense coloration of the resulting particles and the reduced number of washing steps required to remove the excess unincorporated dye, an explanation being the physical entrapment of Nigrosin in the polymer particle.

Photos of the colored particles obtained using the two previously described methods are presented in Figure 5. The colored particles were further functionalized by grafting long alkyl chains onto their surface to provide particle sterical stabilization in nonpolar solvents.

Particle Functionalization and Zeta Potential Measurement. In order to graft sterical chains on the particles, one needs to have functional groups on particle surface. These groups are incorporated directly during the dispersion polymerization by adding a second monomer: methyl methacrylate, or acrylic acid at the end of the styrene polymerization. After washing three times with EtOH followed by centrifugation and drying under vacuum overnight, the PS/DVB-PMMA or the PS/DVB-PAA particles synthesized in EtOH were recovered as a white powder. These particles were further dyed either by swelling in supercritical

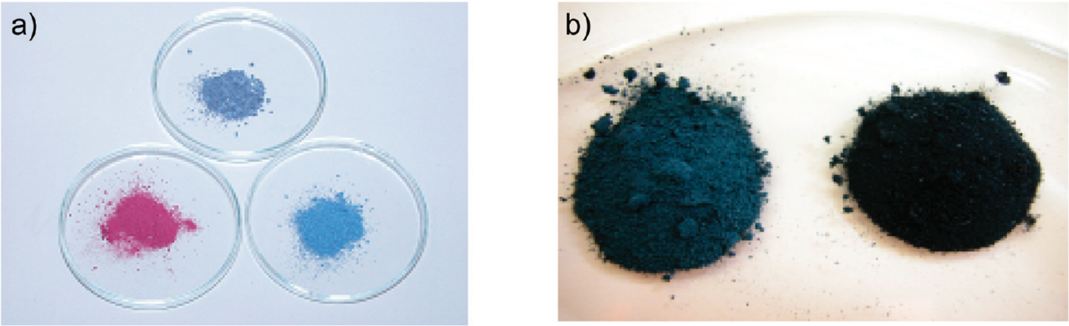


Figure 5. Colored particles. (a) Colored particles obtained after swelling of PS/DVB particles in supercritical CO_2 with Sudan Red, Oil Blue N, and Solvent Blue 35. (b) Dark blue colored PS/DVB particles obtained by swelling in supercritical CO_2 with Sudan Black (left); black PS/DVB particles obtained by dispersion polymerization in presence of Nigrosin (right).

Scheme 4. Grafting Stabilizing Chains of OLOA 1200 on PS/DVB-PMMA Particles via Amidation

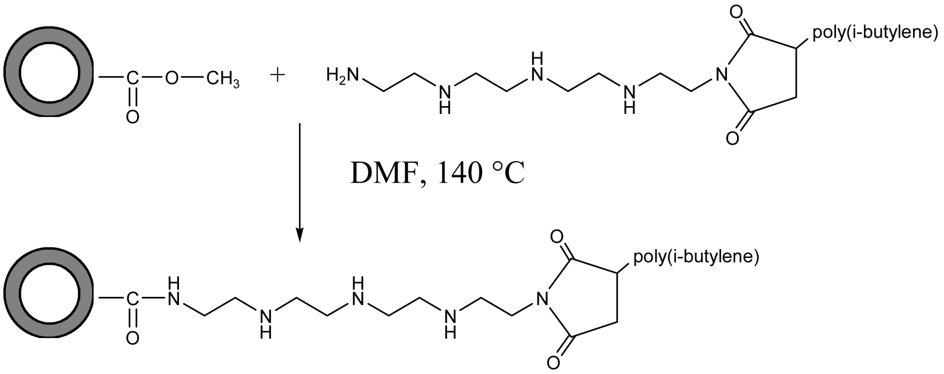


Table 4. Zeta Potential Values at pH 6 Measured in Water for the Synthesized Particles

particle	zeta potential (mV)
PS/DVB	−15.8 (± 0.91)
PS/DVB-PMMA	−12.3 (0.62)
PS/DVB-PMMA-OLOA	+16.1 (0.84)
PS/DVB-PAA	−47.5 (0.98)
PS/DVB-PAA-Kraton	−47.0 (1.29)

CO_2 with different dyes, or by adapting the polymerization method for the incorporation of Nigrosin, resulting in colored particles. In both dyeing methods, the presence of the ester or acid function did not influence particle coloration results.

Two different molecules were grafted at the surface of the particles, giving two different particles, one bearing positive charges, the other bearing negative charges.

We first grafted OLOA 1200, a polyisobutylene succinimide which is a surfactant commonly used in electrophoretic inks. Its amino groups were reacted by amidation with the ester groups already present on the PS/DVB-PMMA particles, as shown in Scheme 4. The reaction was done in DMF as the particles were synthesized in a polar solvent and the surfactant is preferably soluble in nonpolar media. The particles were then washed several times in hexane to remove unreacted OLOA 1200 and dried under vacuum. Finally, they were redispersed in water at pH 6 and their zeta potential was measured (Table 4). After grafting, particle zeta potential shifted from negative to positive values because of the amine functions of the grafted OLOA 1200 chains. A SEM micrograph (Figure 6) shows the final particles after grafting of OLOA 1200.

The second molecule to be grafted on the particles was Kraton L-1203, a hydroxyl terminated ethylene-butylene copolymer. This polymer was grafted on PS/DVB-PAAH particles by esterification in the presence of coupling agents: dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP), in DMF (Scheme 5). SEM micrographs (Figure 7) show the final particles after grafting of Kraton L-1203 and dyeing.

The PS/DVB-PAA particles have negative zeta potential values before and after grafting due to an excess of acrylic acid groups on particle surface. Zeta potential values in mV of the starting particles and zeta potential of particles after functionalization are given in Table 4. The standard deviation values are shown in the parentheses.

It would be expected that the nonfunctionalized PS/DVB and PS/DVB-PMMA particles should not show any electrophoretic behavior because they contain no chargeable groups. The negative charge of the nonfunctionalized particles PS/DVB with $\zeta = -15.8$ mV, PS/DVB-PMMA with $\zeta = -12.3$ mV could be due to the presence of hydroxyl anions that preferentially adsorb onto hydrophobic surfaces in water, creating a negative charge.[31] The values obtained for the zeta potential measurement are a good indication that the final particles really bear the intended functional groups that were grafted on their surface. However, it does not depict the zeta potential of the particles in non polar

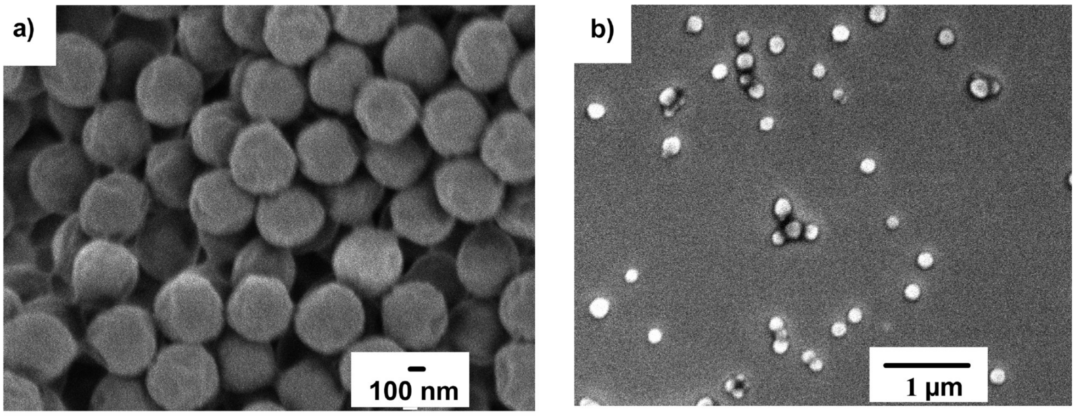
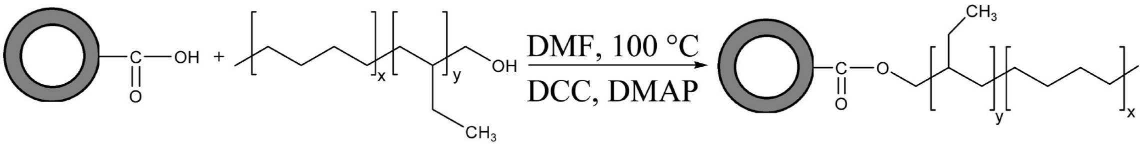


Figure 6. SEM micrographs of PS/DVB-PMMA-OLOA particles: dyed with Sudan Black in supercritical CO_2 (left); Nigrosin dyed PS/DVB-PMMA, with grafted OLOA (right).

Scheme 5. Grafting Stabilizing Chains of Kraton L-1203 on PS/DVB-PAA via Esterification; Poly(ethylene glycol) (a), Poly(propylene glycol) (b)



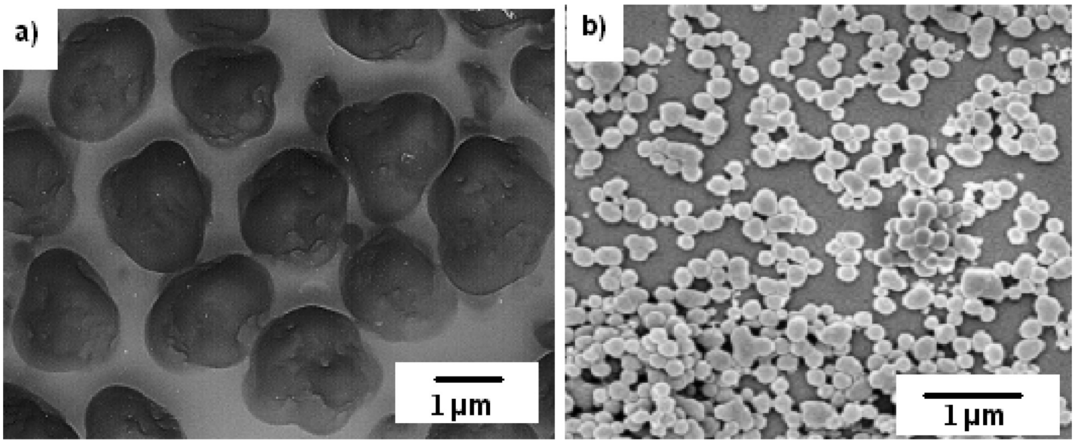


Figure 7. SEM micrographs for PS/DVB-PAA-Kraton particles: dyed with Sudan Black in supercritical CO_2 (left); Nigrosin dyed PS/DVB-PAA, with grafted Kraton (right).

Table 5. Concentration of Compounds in the Dual-Particle Electrophoretic Dispersions

	compd	conc. (mg mL^{-1})
white particle	TiO_2/PS-PMMA-OLOA	40.0
black particle	PS-PAA-Kraton	60.0
dispersing medium	Marcol 52	

media, which will be different because of the difference in dielectric constant.

Electrical and Optical Characterization of Electrophoretic Dispersions. A dual-particle electrophoretic ink with negatively charged colored particles and positively charged white particles was prepared using the formulation described in Table 5. The ink contained no added surfactant, both particle types being stabilized by long alkyl chains grafted on their surface. The ink was introduced in an electrophoretic test-cell (see Experimental Section) for electrical and optical characterization under use. The optical and electrical responses of the tested dispersion are presented in Figure 9.

The results presented here concern black PS-PAA-Kraton particles dyed by dispersion polymerization in presence of Nigrosin and white multilayered electrophoretic particles, based on the light scattering pigment TiO_2. The pigment was encapsulated in PS/DVB by precipitation polymerization as described in a previous article[19] and the particle surface was functionalized with PMMA. The multilayered white core−shell particles were subsequently modified by covalently attaching OLOA 1200 grafts onto particle surface by amidation of the acrylate groups present on particle surface, as described in the Experimental Section. SEM image of these particles is shown in Figure 8.

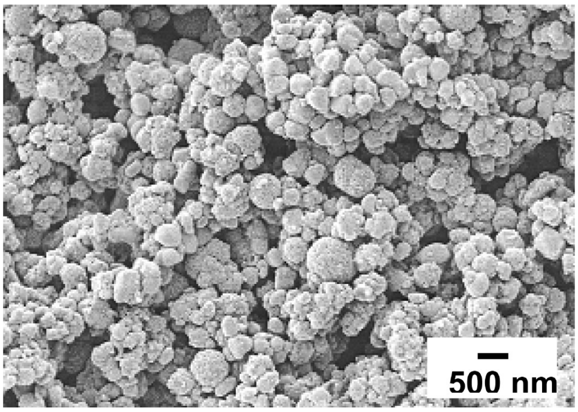


Figure 8. SEM micrograph for TiO_2−PS/DVB-PMMA-OLOA particles.

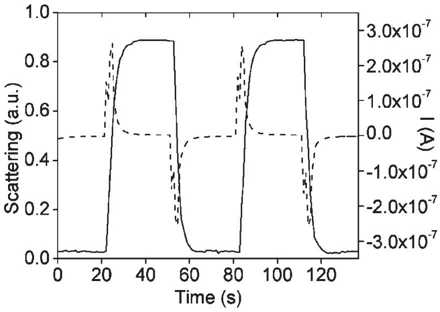


Figure 9. Optical (plain line) and electrical (dashed line) response of an electrophoretic cell containing electrophoretic dispersion of black PS-PAA-Kraton particles and white TiO_2/PS-PMMA-OLOA particles switched at 30 V. The polarity of the applied electrical field is alternated.

Figure 9 shows the optical response (scattering intensity) and electrical response (current intensity) of the electrophoretic display containing dual black and white particle electrophoretic dispersion operated at a constant bias of 30 V. The direction of the applied field is changed every 25 s.

When the white particles have migrated to the front of the electrophoretic test-cell, the light is scattered by the pigments and the cell appears white. On the contrary, when the black particles have migrated to the front of the display, the light is absorbed by the Nigrosin contained in the black particles and the display appears black (Figure 10). The contrast, defined as the ratio between the maximum scattering intensity, measured for the white state and the minimum scattering intensity measured for the black state is 32.

The particles are stable and the scattering levels remain the same during repeated switching cycles, showing that neither irreversible adsorption on the electrodes nor cationic/anionic particles aggregation occurs in the display. Furthermore, the absence of surfactant in the ink allows for low residual current of only a few nanoamps and thus for low power consumption.

■ CONCLUSION

Multilayered colored electrophoretic particles suitable for use in dual-particle electronic inks were prepared via dispersion polymerization of styrene/divinylbenzene followed by polymerization of methyl methacrylate/acrylic acid in a second step. The acrylate and acrylic acid groups on the particle surface enable the grafting of steric moieties that enhance particle stability in nonpolar solvent.

PS/DVB-PMMA particles were functionalized by amidation with amino groups of the OLOA 1200 which, besides positively charging the particle, also plays a role in particle sterical stabilization in the electrophoretic dispersion. PS/DVB-PAA negatively charged particles were functionalized by esterification with the hydroxyl groups of Kraton L-1203 that was grafted on particle surface for sterical stabilization in the electrophoretic dispersion.

Colored particles were obtained by two methods: particle swelling with Sudan Red, Sudan Black, and Solvent Blue 35 in supercritical CO_2 and dispersion polymerization in presence of Nigrosin. The supercritical CO_2 method was influenced by the polarity and the bulkiness of the dye and by polymer particle cross-linking degree. Only slightly cross-linked particles with

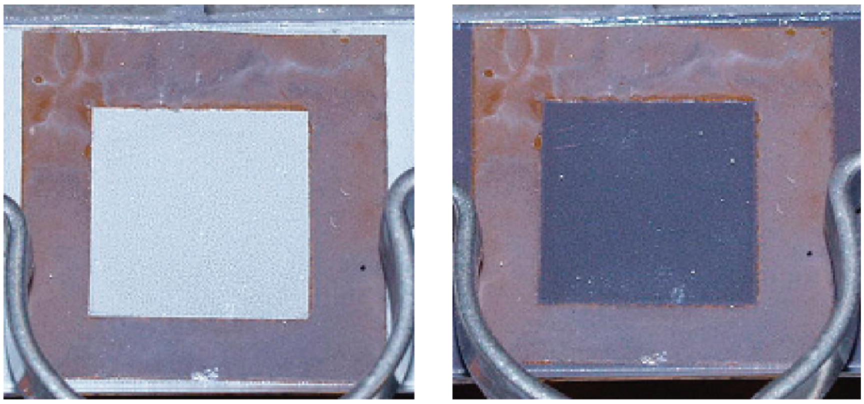


Figure 10. ITO/glass-ITO/glass testcell filled with electronic ink based on countercharging black and white particles (TiO_2−PS-PMMA-OLOA and PS-PAA-Kraton dyed in the presence of black dye Nigrosin, no extra OLOA added). Image of the electrophoretic white/black switch: operating voltage, 30 V; thickness of the spacer, 50 μm.

0.75−1.5 wt % DVB could be swelled in supercritical CO_2, the resulting colored monodisperse particles not showing any change in particle size, size distribution, and morphology.

The dispersion polymerization in the presence of Nigrosin resulted in black monodisperse particles with more important amount of dye incorporation, but with a decrease in polymerization yield and particle size down to 200−300 nm, as compared to the 1.7 μm diameter particle obtained in the absence of dye. After thorough particle washing to remove the unincorporated dye and any unattached surfactant, the zeta potential of the particle was measured in water, at pH 6. The PS/DVB-PAA particles reached a zeta potential of −47.5 mV while PS/DVB-PMMA particles grafted with OLOA acquired a positive surface charge of +16.1 mV.

The synthesized particles were used in the preparation of dual-particle electronic inks against white multilayered core−shell particles based on TiO_2. The optical results showed that no electrode adsorption or particle aggregation occurred in the electrophoretic cell, leading to stable cell color over multiple switching cycles and high optical contrast. The electrical measurement showed very low residual currents of only a few nanoamps and hence low power consumption.

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