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Encapsulation of TiO_2 in poly(4-vinyl pyridine)-based cationic microparticles for electrophoretic inks

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ABSTRACT

Poly(4-vinyl pyridine) microparticles were prepared via surfactant-free emulsion polymerization in water with divinylbenzene as crosslinking agent. The synthesis was adapted for the encapsulation of TiO_2. The size, integrity and nature of the resulting hybrid microparticles were investigated by Scanning electron microscopy, Dynamic light scattering and Fourrier-transform infrared Spectroscopy measurements. The particles were quaternized using a modified copolymer, which was grafted via an alkylation reaction on particle surface followed in a second step by alkylation with methyl iodide. After quaternization, an electrophoretic ink was formulated using the TiO_2/poly(4-vinyl pyridine) cationic microparticles. Under electric field, the electrophoretic ink showed good optical properties, lifetime and stability.

1. Introduction

The electrophoretic image display (EPID) is a reflective-type panel, which is based on electrophoresis. Electrophoresis is the movement of charged entities suspended in a liquid under the influence of an electric field. This phenomenon, first observed by Reuss in 1809 for clay particles suspended in water, has been applied technologically in processes like the analysis or separation of high molecular compounds such as proteins or the electrophoretic deposition [1]. The first EPID has been introduced in 1973 by Ota et al. [2] but the research has progressed so rapidly in the last decade that the first products are appearing on the market at this moment.

The EPID is composed of two transparent and conductive polymer layers containing a suspension of particles in an apolar solvent, also called the electrophoretic ink. On application of an electric field between the electrodes, the particles migrate to the front or to the back of the device. In our set up, white particles are dispersed in a dark blue-dyed apolar solvent. When the particles are at the front electrode, they scatter the light (white state) and when the particles are at the back electrode, the solvent absorbs the light (dark state). The optical properties of an EPID [3–5]: the reflectivity and contrast, are mainly determined by the electrophoretic ink composition. Important criterions are the pigment particles (composition, size, light scattering properties, density), the charges on the particles and the concentration of the different compounds (dye and pigment) as a function of the thickness of the device. To obtain a working electrophoretic dispersion, pigments such as TiO_2 or dyes have to be encapsulated in a polymer shell in order to prevent sedimentation of the particles and carry the highest negative or positive charge as possible to ensure a fast response time of the display. Moreover, they should be sterically stabilized to improve the lifetime of the display by grafting long hydrophobic chains on particle surface.

We focus here on the synthesis of cationic particles. These particles are usually prepared by surfactant-free emulsion copolymerization of styrene with quaternary ammonium monomers such as diallyldimethylammonium chloride (DADMAC), methacryloyloxyethyl trimethyl ammonium chloride (MOTAC) and vinyl benzyl trimethyl ammonium chloride (VIBTAC) [6–8]. These monomers provide permanent positive charge to the particles but their introduction also results in the formation of water-soluble polyelectrolyte, which then leads to the flocculation of the latex [9]. Moreover, the particles are not sterically stabilized, as is required for our application.

Voorn et al. [9] prepared cationic particles in two steps, first the surfactant free polymerization of glycidyl methacrylate and butyl methacrylate, followed by the aminolysis of epoxy groups into quaternary ammonium groups, with a good control of the charge densities and negligible formation of water-soluble polyelectrolyte.

Like Voorn et al., we present the preparation of cationic particles in two steps: first the surfactant-free emulsion polymerization of 4-vinyl pyridine, crosslinked with divinylbenzene,

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followed by quaternization of the polymer and grafting of hydrophobic chains on their surface to provide positive charges and steric stabilization. 4-Vinyl pyridinium salts cannot be used directly in controlled emulsion polymerization as quaternization of 4-vinyl pyridine monomer leads to spontaneous polymerization [10]. However, several teams described the surfactant-free emulsion polymerization of 4-vinyl pyridine [11–13]. Moreover, it was shown that poly(4-vinyl pyridine) can also be quaternized with different alkylation agents after the polymerization [14], methyl iodide being a reagent favoring high quaternization yields [10].

The originality of our work is the quaternization of the particles first in a bad solvent with long hydrophobic halogenide molecules to functionalize the surface of the particles with long alkyl chains. Then, quaternization is carried on in a good solvent with methyl iodide that can enter the swollen particle and increase the charge density of the particles.

Once the synthesis of the particles and their quaternization were optimized, TiO_2 was encapsulated in poly(4-vinyl pyridine). Finally, the TiO_2–PVPy particles were optically tested in electrophoretic dispersions.

2. Experimental section

2.1. Materials

Divinyl benzene was purchased from Aldrich and passed over a column of basic aluminium oxide before use to remove inhibitor. The isomer mixture of vinylpyridine 95% was purchased from Acros. Iodooctadecane 95% and potassium persulfate were purchased from Aldrich and used without further purification. Methyl iodide 99% was purchased from Avocado. Kraton L-1203 (hydroxyl terminated hydrogenated ethylene–butylene copolymer), $M_n = 7600\ g\ mol^{-1}$ (measured by gel permeation chromatography in tetrahydrofuran with polystyrene standards) was offered by Shell Chemicals and was dried before use. TiO_2 RL-11A was offered by Millennium Chemicals (particle size 230 ± 50 nm as measured by DLS). Sudan Blau Flüssig (an oil soluble organic colorant) was received from BASF and Marcol 52 (a paraffinic oil) was received from ESSO. Toluene was obtained from Aldrich and distilled from CaH_2. Phosphorus pentachloride was purchased from Merck.

2.2. Synthesis of PVPy particles

A 250 ml three-necked flask, equipped with a mechanical Teflon stirrer with half-moon shaped pallets and nitrogen inlet, is charged with distilled water (110 ml). A mixture of 4-vinyl pyridine (10 ml) and divinylbenzene (1 ml) is prepared in a separate flask and added to the reaction mixture. After 20 min of homogenization, at 300 rpm and 80 °C, potassium persulfate (0.1 g) dissolved in distilled water (5 ml) is added to the reaction flask. The reaction mixture is then stirred for 3 h under nitrogen. After this time, the system is allowed to cool down to room temperature. The particles are washed twice with hexane and twice with chloroform by centrifugation at 3000 rpm for 15 min, followed by replacement of the supernatant and redispersion in the solvent. The particles are finally dried under vacuum and analyzed by FT-IR.

2.3. Synthesis of TiO_2/PVPy particles

In a three-necked 250 ml flask, equipped with a mechanical Teflon stirrer and nitrogen inlet, TiO_2 (5 g) is dispersed in distilled water (110 ml) and ultrasonicated for 60 min in an ultrasonic water bath (170 W). A mixture of vinylpyridine (5 ml) and divinylbenzene (1 ml) is prepared in a separate flask, and added to the reactor. After 20 min of homogenization, at 300 rpm and 80 °C, 0.1039 g potassium persulfate dissolved in 5 ml distilled water is added to the reaction mixture, which is stirred for 3 h under nitrogen. After this time, the system is allowed to cool down to room temperature.

The particles are centrifuged at 3000 rpm for 15 min and washed with hexane and chloroform as described previously. The particles are finally dried under vacuum.

2.4. Modification of Kraton

The Kraton used is a hydroxyl terminated hydrogenated ethylene–butylene copolymer. In order to use it as a quaternization agent for poly(4-vinyl pyridine), the hydroxyl function is replaced by a chloride as follows. A 100 ml round bottom flask equipped with reflux condenser is placed under inert atmosphere. Dried Kraton L-1203 (10 g) is dissolved in toluene (40 ml). PCl_5 (1 g) is then added to the flask under stirring. The mixture becomes bright yellow. The reaction is stirred overnight at room temperature. Toluene is then evaporated and the polymer dissolved in chloroform. It is washed several times with a NaCl saturated solution, then with a sodium hydrogen carbonate solution. After separation, the organic phase is dried on $MgSO_4$, filtered and the excess solvent is evaporated. An FT-IR analysis shows the disappearance of the starting material OH characteristic band from 3000 to 3500 cm^{-1}, indicating that the functionalization succeeded.

2.5. Alkylation of the PVPy particle surface

A 50 ml round bottom flask with reflux condenser is placed under inert atmosphere. The dried synthesized PVPy particles (2 g) and 5 g of modified Kraton chloride are placed in 20 ml hexane. The mixture is stirred at 50 °C for 24 h. At the end of the reaction, the system is allowed to cool down to room temperature. The particles are recovered by filtration and washed successively with dichloromethane and hexane. The obtained particles are dried under vacuum and characterized by FT-IR.

2.6. Alkylation of PVPy particle core

A 50 ml round bottom flask with reflux condenser is placed under inert atmosphere. The dried PVPy particles (1 g) obtained from the previous alkylation step and 8 g of methyl iodide are placed in 20 ml dichloromethane. The mixture is stirred at room temperature for 4 h. At the end of the reaction, the particles are recovered by filtration and washed successively with dichloromethane and hexane. The obtained particles are dried under vacuum and characterized by FT-IR.

2.7. Particle characterization

Zeta potential of the particles in water at pH 6, was measured using a zetameter (Zetasizer 2000 from Malvern Instruments). Dynamic light scattering (DLS) measurements were performed using Zetasizer 2000 from Malvern Instruments.

2.8. Electro-optical characterization

Electrophoretic dispersions are prepared by dispersion of the synthesized particles in Marcol, in the presence of a dye, the Sudan Blau Flüssig. It is then introduced in an electrophoretic cell, composed of two ITO-covered glass slides (2 × 3 cm) separated by a 50 μm-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 we have measured the light scattering under a 0° angle with a silicon

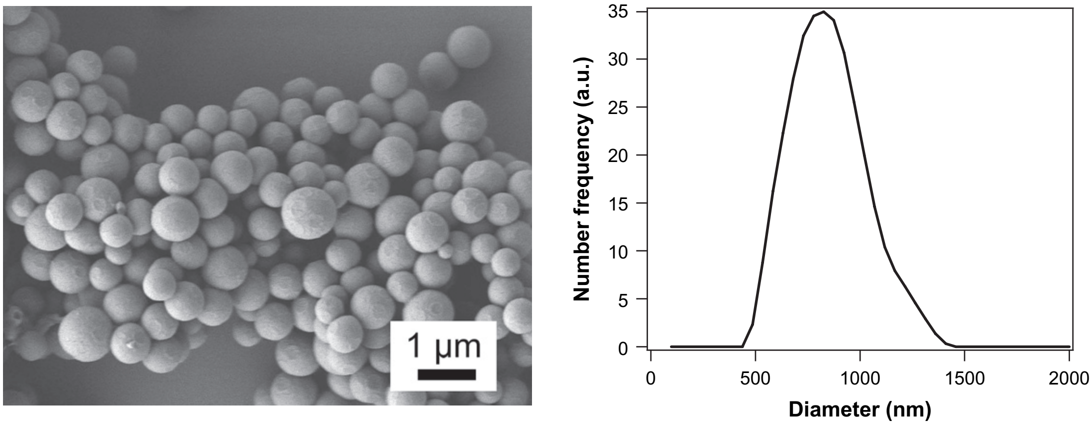


Fig. 1. SEM micrograph of PVPy/DVB particles A1 (left) and their number size distribution curve (right).

photodiode. Illumination was under an angle of 30° with a 4 mW He/Ne laser ($\lambda = 664$ nm) [15].

3. Results and discussion

3.1. *Synthesis of poly(4-vinyl pyridine) polyelectrolyte particles via emulsion polymerization in water*

Poly(4-vinyl pyridine) particles, crosslinked with divinylbenzene (PVPy/DVB), are first synthesized by surfactant-free emulsion polymerization in water in one step.

The obtained crosslinked particles and the particle size distribution are presented in Fig. 1.

The emulsion polymerization of 4-vinyl pyridine in water results in polydisperse particles in the range 500–1000 nm (Table 1). By increasing the stirring rate from 300 to 600 rpm the particle size does not change significantly, which is characteristic of emulsion polymerization. This process is then further applied to the encapsulation of TiO_2 in polymer, as represented in Scheme 1. In this case, heteronucleation occurs at the surface of the particles and TiO_2 is encapsulated in a poly(4-vinyl pyridine) shell.

Table 1
Influence of different reaction parameters on the synthesis of PVPy particles and core–shell TiO_2–PVPy particles

Entry	Synthesized particle	Monomer (wt%)	TiO_2/ monomer	Reaction time (h)	Stirring (rpm)	Particle size[a] (nm)
A1	PVPy	10	–	3	300	750 ± 190
A2	PVPy	10	–	3	600	630 ± 300
B1	TiO_2–PVPy	10	1:1	8	300	320 ± 60
B2	TiO_2–PVPy	5	1:1	8	300	470 ± 130
B3	TiO_2–PVPy	5	1:1	24	300	520 ± 200
B4	TiO_2–PVPy	5	2:1	24	300	330 ± 100
B5	TiO_2–PVPy	5	1:2	24	300	910 ± 210

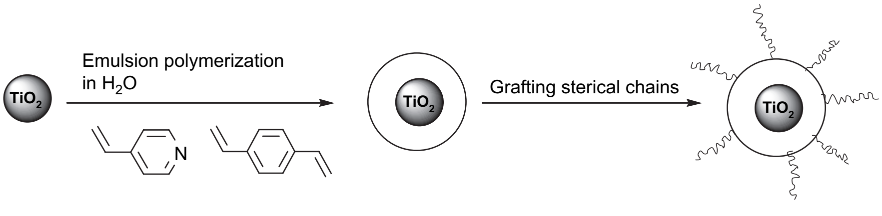
[a] Particle size as determined by DLS.

The influence of monomer weight percentage with respect to solvent amount, the ratio pigment:polymer and reaction time is studied (Table 1). For the encapsulation of TiO_2 in PVPy, it was found that the polymer shell increased in thickness by extending the reaction time from 8 to 24 h and the particles remained polydisperse (entry B2 and B3). Decreasing the monomer concentration does not change significantly the particles size (entry B1 and B2). However, the particles size increases when the TiO_2 to monomer ratio decreases, which suggests that TiO_2 acts as a seed and therefore should be well encapsulated. Polymerization yields, measured after evaporation of water and of the remaining monomers, are superior to 95% for all experiments.

Scanning electron micrographs of the TiO_2–PVPy particles and the size distribution curves are presented in Fig. 2. The TiO2 particles used in this study are non-spherical. After encapsulation by PVPy, their size increases but they keep their non-spherical shape.

3.2. *PVPy particle alkylation*

Our objective was to obtain cationic sterically stabilized particles using hydrophobic chains. For this purpose, the particles were alkylated. The particle alkylation consists in the quaternization of the polyvinylpyridine nitrogen atom in order to obtain a polyalkylvinylpyridinium salt. For a total alkylation, the particles underwent two reaction steps. The first step involved a long chain hydrophobic agent dissolved in hexane. Hexane is a bad solvent for the crosslinked polyvinylpyridine particles which do not swell, therefore the alkylation was effective mainly at the surface. We chose to use Kraton L-1203, which is long enough to ensure a good steric stabilization and modified it by halogenation of the end group, according to Scheme 2. It is then compared with the alkylation with iodooctadecane, which has a smaller hydrophobic chain. The second alkylation step was done in dichloromethane, a good solvent for the polymer particle, in which the particles swell. We used a more reactive alkylating agent, methyl iodide, in order to have good alkylation of the polymer particles, even in volume. The



Scheme 1. Encapsulation of TiO_2 in PVPy during surfactant-free emulsion polymerization of 4-VPy in water.

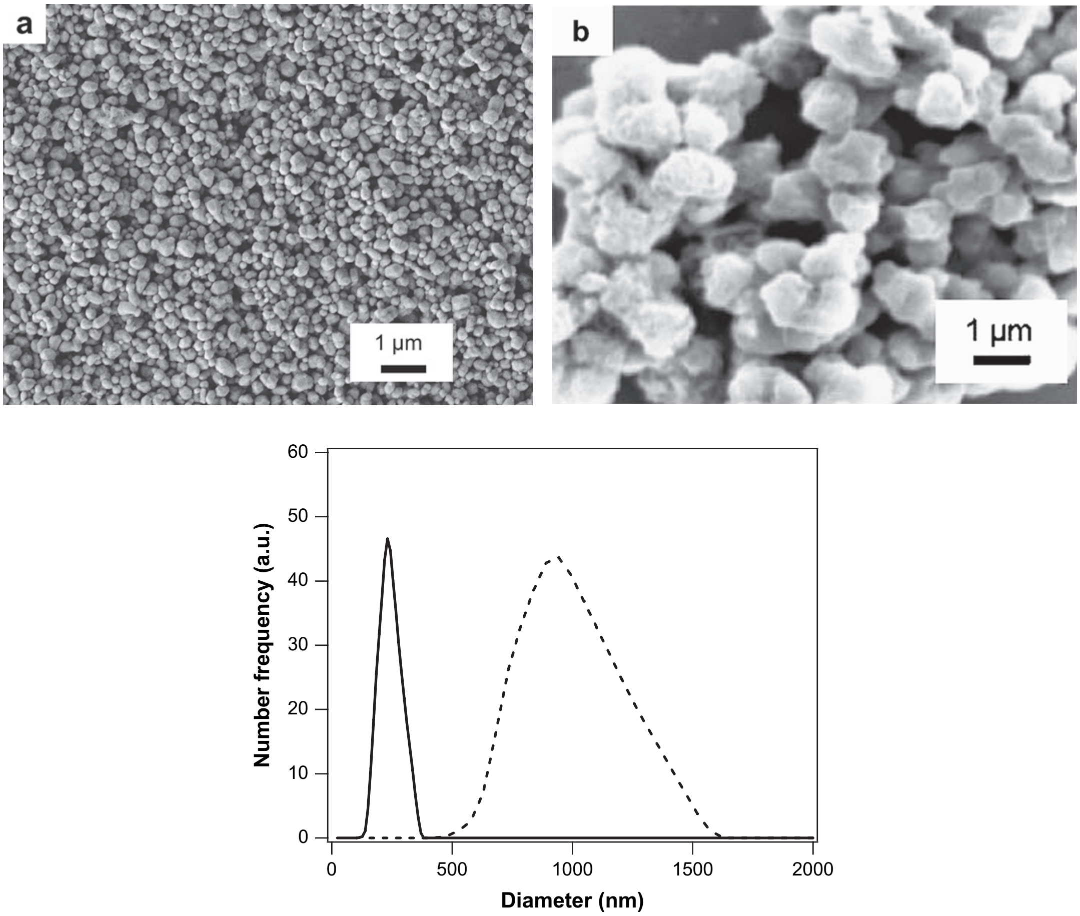
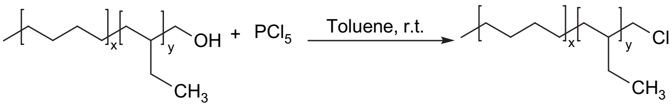


Fig. 2. SEM micrographs of crude TiO_2 (a) and TiO_2/PVPy (b) particles. Number size distribution curves for the TiO_2 (plain line) and TiO_2/PVPy particles (dashed line, entry B5) measured by DLS.

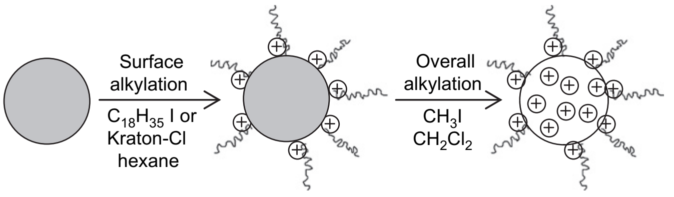
global alkylation of the polyvinylpyridine particle is schematically shown in Scheme 3 and the reaction path in Scheme 4.

A comparison between infrared spectra of PVPy particles before and after quaternization using modified Kraton shows an increase of the peaks in the region 2800–3000 cm^{-1} which is specific for the C–H bonds, indicating the presence of the polyolefin chain of the modified Kraton.

Particle zeta potential in NaCl 10^{-3} M was measured for the starting pigment particles and the final electrophoretic particles, obtained after the different functionalizations. The results are presented in Table 2.

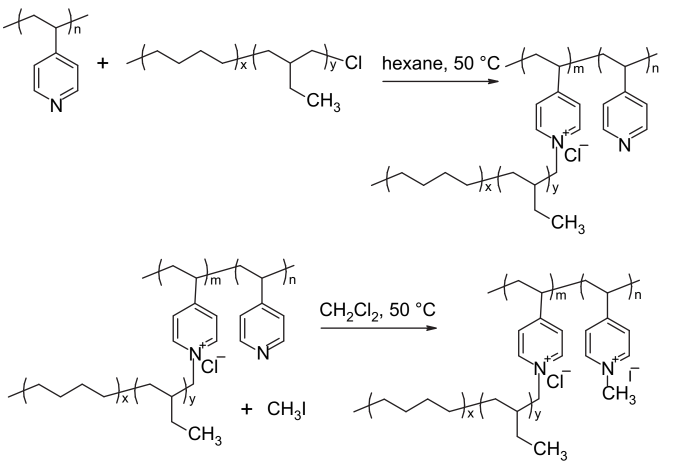


Scheme 2. Modification of Kraton L-1203 end group.



Scheme 3. Schematic representation of the PVPy particle quaternization.

The PVPy particles are negatively charged, with a zeta potential of −2.3 mV. After the first alkylation step it becomes neutral or positive depending on the alkylating agent used. Alkylation with $C_{18}H_{35}I$ seems to be less effective than alkylation with Kraton-Cl. This could be due to non-optimized experimental conditions or to a difference in affinity of the two molecules with the particles' surface. After the second alkylation step with CH_3I both particles become clearly positive. This means that alkylation is completed



Scheme 4. Chemical reaction steps towards the overall quaternization of PVPy.

Table 2
Electrophoretic characterization of cationic particles

Starting particle	Zeta potential (mV)	Final particle	Zeta potential (mV)
TiO_2	−21.7		
PVPy	−2.3		
TiO_2–PVPy	−8.5		
TiO_2–PVPy–$C_{18}H_{35}$	−1	TiO_2–PVPy–$C_{18}H_{35}$–CH_3	+28.2
TiO_2–PVPy–Kraton	+9.2	TiO_2–PVPy–Kraton–CH_3	+36.5

Table 3
Composition of the electrophoretic dispersion

Component	Compound	Concentration ($mg \cdot ml^{-1}$)
Pigment	TiO_2–PVPy–Kraton	40.0
Dye	Sudan Blau Flüssig	20.0
Fluid medium	Marcol 52	–

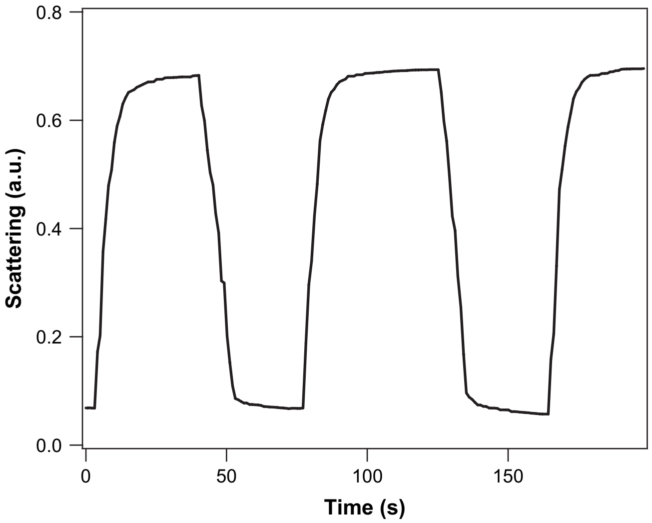


Fig. 3. Optical response of an electrophoretic ink, formulated with core–shell TiO_2–PVPy quaternized particles.

both in the particle core and on the surface. For the fully alkylated particles the zeta potential is as high as +36.5 mV.

3.3. *Optical characterization of electrophoretic dispersion*

The synthesized TiO_2–PVPy–Kraton core–shell particles were used for the preparation of a novel electrophoretic ink. An electrophoretic cell, consisting of two ITO-glass electrodes distanced by a 50 μm inert spacer, was filled with a dispersion having the composition showed in Table 3. Electro-optical characterization of the cell is performed as described in Section 2.

Fig. 3 shows the optical response at an applied voltage of 30 V. The direction of the applied field is changed alternatively. Starting from a homogeneous system, the particles are moved to the front electrode in the first switch, and the reflectance increases rapidly (light scattering particles at the top, viewing electrode). After reaching the white state, the direction of the field is changed, the particles move to the back electrode leading to a dark state. The light is absorbed by the colored dispersion medium.

The obtained contrast, defined as the ratio between reflected light in the white state and dark state, is 9, a value comparable to current newspapers.

The constant level of the black and white states during the successive measuring cycles and the good contrast indicate that no permanent adsorption of the TiO_2/PVPy particles at the electrodes occurs. These results confirm the effective encapsulation of the pigments with PVPy and their good steric stabilization.

4. Conclusion

Sterically stabilized cationic particles are prepared in two steps. The first step is the surfactant-free emulsion polymerization of poly(4-vinyl pyridine) (PVPy). This procedure is then applied to the encapsulation of TiO_2. We showed that the thickness of the polymer layer can be varied by adjusting the TiO_2 to monomer ratio. In the second step, the particles are charged by functionalization of their surface with long alkyl quaternization agents in a poor solvent for PVPy, followed by functionalization of the particle core with methyl iodide after swelling in good solvent. Thus, the resulting particles are both electrically charged and sterically stabilized. After alkylation, the zeta potential of the particles shifts from negative to positive values, which confirms the formation of pyridinium salt. Optical measurements are performed on a formulation of an electrophoretic ink, composed of the prepared particles in a paraffinic oil and a contrasting blue dye. The obtained contrast, defined as the ratio between reflected light in the white state and dark state, is 9 with a good stability of the dark and white states, which proves that the particles are well stabilized and do not adsorb onto the electrodes.

References

[1] Van der Biest OO, Vandeperre LJ. Annual Review of Materials Science 1999;29:327–52.
[2] Ota I, Onishi J, Yoshiyama M. Proceedings of the IEEE 1973;61(N7):832.
[3] Comiskey B, Albert JD, Yoshizawa H, Jacobson J. Nature 1998;394:253–5.
[4] Jacobson J, Jonathan A, Comiskey B. WO patent 9841899; 1998.
[5] Werts MPL, Badila M, Brochon C, Hébraud A, Hadziioannou G. Chemistry of Materials 2008;20:1292–8.
[6] Liu Z, Xiao H, Wiseman N. Journal of Applied Polymer Science 2000;76:1129–40.
[7] Liu Z, Xiao H. Polymer 2000;41:7023–31.
[8] Dziomkina NV, Hempenius MA, Vancso GJ. European Polymer Journal 2006;42:81–91.
[9] Voorn D-J, Ming W, van Herk AM. Macromolecules 2005;38:3653–62.
[10] Chovino C, Gramain P. Polymer 1999;40:4805–10.
[11] Pathak S, Greci MT, Kwong RC, Mercado K, Prakash GKS, Olah GA, et al. Chemistry of Materials 2000;12:1985–9.
[12] Li G, Shen J, Zhu Y. Journal of Applied Polymer Science 2000;78:668–75.
[13] Ma Q, Gu L, Ma S, Ma G. Journal of Applied Polymer Science 2002;83:1190–203.
[14] Bicak N, Gazy M. Journal of Macromolecular Science 2003;A40(6):858.
[15] Groenewold J, Dam MA, Schroten E, Hadziioannou G. Proceedings of the Society for Information Display 2002;33:671.