Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Electronic Ink Particles for Electronic Paper by Polymerization Method

Hyo Sim Kang [a], Hwa Jin Cha [a], Ju Chang Kim [a], Mi Na Park [a], Young Soo Kang [a] & Sun Wha Oh [b]

[a] Department of Chemistry, Pukyong National University, Busan, Korea

[b] Basic Science Research Institute, Pukyong National University, Busan, Korea

Version of record first published: 22 Sep 2010

To cite this article: Hyo Sim Kang, Hwa Jin Cha, Ju Chang Kim, Mi Na Park, Young Soo Kang & Sun Wha Oh (2007): Synthesis and Characterization of Electronic Ink Particles for Electronic Paper by Polymerization Method, Molecular Crystals and Liquid Crystals, 472:1, 247/[637]-254/[644]

To link to this article: http://dx.doi.org/10.1080/15421400701547920

Mol. Cryst. Liq. Cryst., Vol. 472, pp. 247/[637]–254/[644], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701547920

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of Electronic Ink Particles for Electronic Paper by Polymerization Method

Hyo Sim Kang
Hwa Jin Cha
Ju Chang Kim
Mi Na Park
Young Soo Kang
Department of Chemistry, Pukyong National University, Busan, Korea

Sun Wha Oh
Basic Science Research Institute, Pukyong National University, Busan, Korea

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline nanoparticles with sizes ranging from tens to hundreds of nanometers were prepared by the reprecipitation method and polymerized with methyl methacrylate and ethylene glycol dimethacrylate using surfactants. The electronic ink particles of pyrazoline organic nanoparticles were successfully prepared by dispersion polymerization in aqueous alcohol medium for full color electronic paper, which is expected to substitute for the future display. In order to improve their mobility, the surfactant was added as a charge control additive. The electrophoretic mobility of the resulting electronic inks was $3.059 \times 10^{-4}\,cm^2/V \cdot s$ *in the presence of 3 wt% surfactants.*

Keywords: e-paper; organic nanoparticles; pyrazoline; reprecipitation method

INTRODUCTION

Nanoparticles of semiconductors and metals have been an extremely active area of research because of their interesting quantum confinement effect on optical and electronic properties [1–3]. However, studies of organic nanoparticles have been paid little attention. Due to

This work was financially supported by Brain Korea 21.

Address correspondence to Young Soo Kang, Department of Chemistry, Pukyong National University, 599-1 Daeyeon-3-dong, Nam-gu, Busan 608-737, Korea. E-mail: yskang@pknu.ac.kr

the much more structural diversity and complexity of organic molecules, the current tendentious extension of the research from nanosized inorganic to organic semiconducting materials [4–6] is expected to create a wide range of new size-dependent properties of organic nanoparticles for promising organic optoelectronic devices in a cost-effective way. In this study, motivated by the attractive potentials of fluorescent organic nanoparticles particularly for the nanosized optoelectronic devices applications, we have engaged in the preparation of electronic ink particles using pyrazoline nanoparticles. Polymerization of pyrazoline nanoparticles by methyl methacrylate and ethylene glycol dimethacrylate was investigated in aqueous ethanol medium to get stabilized organic nanoparticle for the easy application materials in the electronic papers. The dispersion polymerization of methyl methacrylate and ethylene glycol dimethacrylate in a water-methanol medium, with surfactants was investigated to prepare the electronic ink particles using organic nanoparticles for electrophoretic displays. To provide electrophoretic response to the particles, ionic surfactants as charge control additives are necessary. The electrophoretic response of the prepared electronic ink particles is examined. The fabrication and performance of electrophoretic display were also investigated.

EXPERIMENTAL

Materials

4-(Dimethylamino)aldehyde, sodium ethoxide, 2′-acetonaphthone, phenyl-hydrazine, methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), 2,2′-azobis(2-methylpropionamidine) dihydrochloride, 4-vinyl-1-cyclohexene diepoxide and stearic acid were purchased from Aldrich Chemical Co. and used without any further purification. All solvents were obtained from Junsei Chemical Co. and used without further purification. Indium-tin-oxide (ITO) coated glass with sheet resistance of 30 Ω/sq was obtained from Samsung Corning Co.

Preparation of Pyrazoline Nanoparticles

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline was synthesized according to the previous report [8] and conformed by NMR and MS. Its molecular structure is shown in Figure 1. The pyrazoline nanopaticles were prepared by the reprecipitation method [8]. By controlling the quantity of pyrazoline acetone solution injected into water

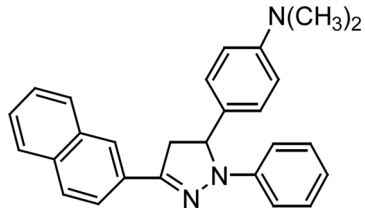

FIGURE 1 The structure of 1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline.

and temperature, the size of nanoparticles was controlled. The fabrication procedure of pyrazoline nanoparticle was previously reported [8].

Procedure of Electronic Ink Particles by Dispersion Polymerization

A solution of methanol (60 mL) and water dispersion of pyrazoline nanoparticles (240 mL, 40 nm) was stirred under N_2 at 60°C. Methyl methacrylate (0.285 mol, 30.2 mL), ethylene glycol dimethacrylate (7.50 mmol, 1.4 mL) and stearic acid (0.47 g) were added into a reaction medium. To a solution 2,2′-azobis(2-methylpropionamidine) dihydrochloride (0.15 g) in water (10 mL) was injected using a glass syringe, and the polymerization was allowed to proceed for 24 h. After the completion of the polymerization process, the reaction mixture was cooled, washed several times with water, and dried in a freeze-drier. In this work, the MMA/EDGMA weight ratio in the monomer mixture was fixed at 95:5. The well dispersed e-particles by polymerization method were obtained.

CHARACTERIZATION OF ELECTRONIC INK PARTICLES

The size and shape of electronic ink particles were observed by means of field-emission scanning electron microscope (FE-SEM: JSM-6700F). The size and its distribution of ink particles were also evaluated by the dynamic light scattering (DLS) technique using a Zetaplus 1246 (Brookhaven Instruments Corporation, USA). The current-applied voltage characteristics of the e-paper display cell were measured with Current/Voltage Source Meter (KEITHLEY2400). The emission fluorescence spectra were recorded with a fluorescence spectrometer (Hitachi F-4500). Zeta potential and mobility of the charged particles

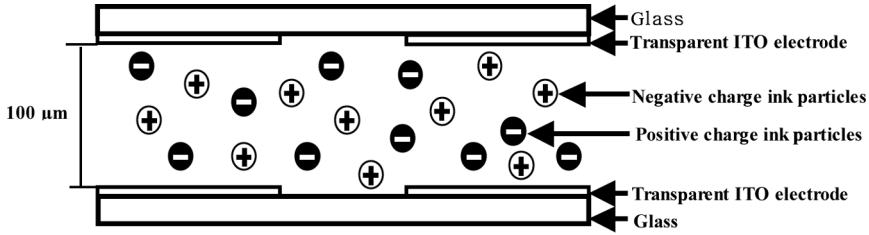

FIGURE 2 Schematic illustration of in-plane electrophoretic display cell.

were measured by zeta potential analyzer (Otsuka electronics, Moedl: ELS-8000).

FABRICATION OF ELECTROPHORETIC DISPLAY

ITO-coated glass with a sheet resistance of 30 Ω/sq was cut into a 3.0×4.0 cm, and the electrode area was prepared by a photoetching technique. It was sequentially cleaned in an ultrasonic bath of isopropyl alcohol, acetone and distilled water, followed by drying it at 120°C. Two ITO-coated glasses were sealed with 100 μm thickness, and a e-ink slurry prepared by mixing ink particle with methanol solvent was injected through the entry port to give rise to the electrophoretic display. The display cell was UV-cured by photo initiator, 4-vinyl-1-cyclohexene diepoxide. Figure 2 shows schematic illustration of in-plane electrophoretic display cell.

RESULTS AND DISCUSSION

We successfully prepared electronic ink particles of pyrazoline organic nanoparticles by dispersion polymerization of methyl methacrylate and ethylene glycol dimethacrylate in a water-methanol medium, with surfactants as charge control additives. Water dispersion of pyrazoline nanoparticles was added to the polymerization systems that contained methyl methacrylate, ethylene glycol dimethacrylate, stearic acid, methanol and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (0.5 wt%). In recent report of electronic ink particles [9,10], the amount of dye in the polymerization feed did not have a significant effect on either the amount of dye in the polymerized particles or the final conversion of monomer and the addition of methanol to the polymerization media did have a dramatic effect on the dye holding or incorporation ability. As methanol fraction was increased up to 20% of volume ratio, the incorporation of dye was improved up to

97% of the theoretical value. In our research, water/methanol volume ratio was fixed at 80:20. The charge control additives are necessary in order to provide electrophoretic response to the electronic ink particles. We selected an ionic surfactant (stearic acid) as a charge control additive because the organic thin film of stearic acid/pyrazoline nanoparticle complex was fabricated by the Langmuir-Blodgett technique in our recent study [7,11]. Electronic ink particles containing surfactants as charge control additives were polymerized in a 80/20 water-methanol mixture which the concentration of stearic acid employed was 3 wt%. Ink particle diameter was under 350 nm. Figure 3 shows FE-SEM images of ink particles prepared using pyrazoline nanoparticles with a surfactant. The ink particles were spherical with uniformly smooth surface. The electronic ink particles with fairly narrow size distributions were obtained. Figure 4 displays the fluorescence emission spectra of pyrazoline monomer in dilute acetone solution (a),

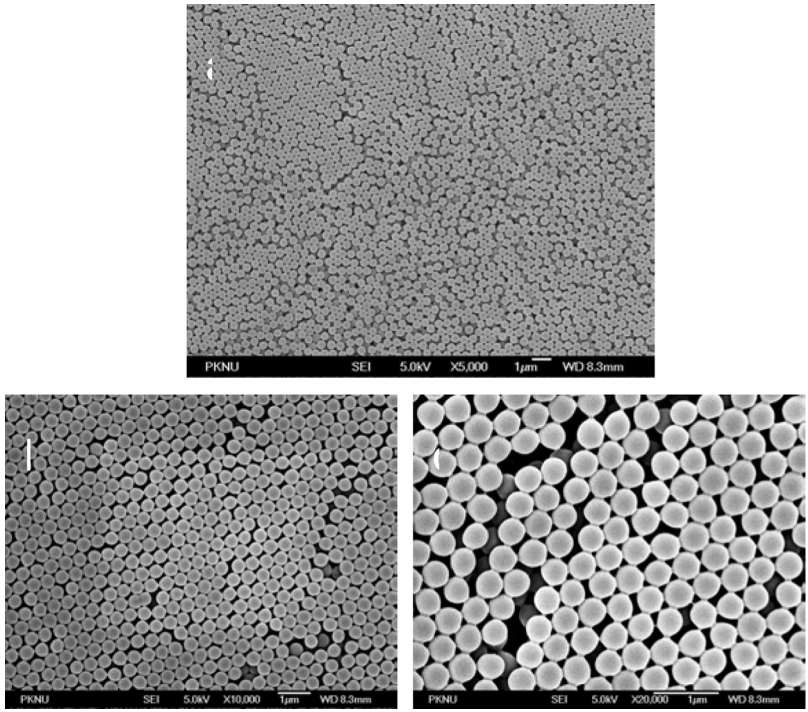

FIGURE 3 The FE-SEM images of electronic ink particles with different magnification (a) ×5,000 (b) ×10,000 (c) ×20,000, their size is from 350 nm to 450 nm.

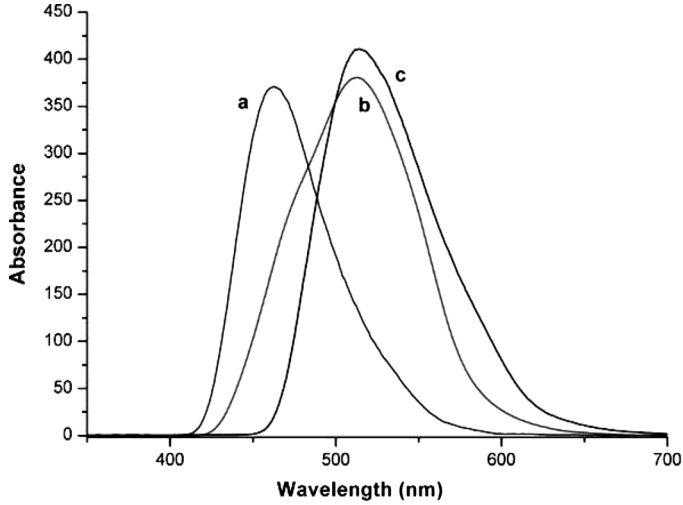

FIGURE 4 The fluorescence emission spectra of (a) pyrazoline molecule, (b) pyrazoline nanoparticle and (c) ink particle.

pyrazoline nanoparticles dispersed in water (b) and electronic ink particles (c). This indicates that electronic ink particles prepared by dispersion polymerization of methyl methacrylate and ethylene glycol dimethacrylate contains pyrazoline nanoparticles. Therefore, the size-dependence of emission exhibited by pyrazoline nanoparticles can be used the fabrication of electronic ink particles for electronic paper applications. The electrophoretic mobility (μ) was calculated by the conversion of the ξ-potential with the Smoluchowski relation, $\xi = \mu\eta/\varepsilon$, ε, where η ($= 1.804$ cP) and ε ($= 24.30$) are the viscosity and dielectric constant of the suspending fluid, respectively. The electrophoretic mobility was measured using a ink particles dispersion, which was obtained by redispersing the synthesized particles after cleaning and drying them. The ink particles in this study were spherical with a uniformly smooth surface. The electrophoretic mobility was $3.059 \times 10^{-4}\,\mathrm{cm^2/V \cdot s}$ at a surfactant content of 3 wt%. Electrophoretic slurry was prepared by blending of ink particles with methanol solvent. The ink particles using 3 wt% surfactant were used for the fabrication of the electrophoretic display cell. Figure 5 shows current-applied voltage characteristics of electrophoretic display cell. The e-paper display panel fabricated with electronic ink particles using pyrazoline nanoparticles exhibited good electrical characteristics.

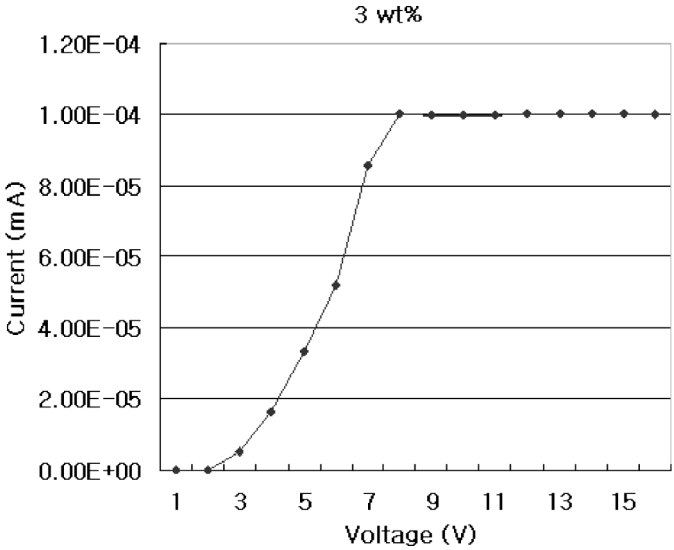

FIGURE 5 The current-applied voltage curve of electrophoretic display.

CONCLUSIONS

The dispersion polymerization of methyl methacrylate and ethylene glycol dimethacrylate using pyrazoline organic nanoparticles in a methanol and water mixture was studied to obtain mono-dispersed electronic ink particles from 350 nm to 450 nm. Adding surfactant as a charge control additive results in electrophoretic mobility. In applications, monodispersed ink particles using organic nanoparticles are expected to be very useful in e-paper displays.

REFERENCES

[1] Colvin, V. L., Schlamp, M. C., & Alivisatos, A. P. (1994). *Nature*, *370*, 354–357.
[2] Artemyev, M. V., Woggon, U., Wannemacher, R., Jaschinski, H., & Langbein, W. (2001). *Nano. Lett.*, *1*, 309–314.
[3] Gu, H. W., Zheng, R. K., Zhang, X. X., & Xu, B. (2004). *J. Am. Chem. Soc.*, *126*, 5664–5665.
[4] An, B. K., Kwon, S. K., Jung, S. D., & Park, S. Y. (2004). *J. Am. Chem. Soc.*, *124*, 14410–14415.
[5] Xu, X. J., Siow, K. S., Wong, M. K., Gan, L. M. (2001). *Langmuir*, *17*, 4519–4524.
[6] Hittinger, E., Kokil, A., & Weder, C. (2004). *Angew, Chem., Int. Ed.*, *43*, 1808–1811.
[7] Oh, S. W. & Kang, Y. S. (2006). *Colloids and Surfaces A*, *284–285*, 359–363.
[8] Oh, S. W., Zhang, D. R., & Kang, Y. S. (2004). *Mater. Sci. Eng. C*, *24*, 131–134.

[9] Yu, D. G., An, J. H., Bae, J. Y., Jung, D. J., Kim, S., Ahn, S. D., Kang, S. Y., & Suh, K. S. (2004). *Chem. Mater.*, *16*, 4693–4698.
[10] Yu, D. G., An, J. H., Bae, J. Y., Ahn, S. D., Kang, S. Y., & Suh, K. S. (2005). *Macromolecules*, *38*, 7485–7491.
[11] Oh, S. W. & Kang, Y. S. (2006). *Mol. Cryst. Liq. Cryst.*, *445*, 259–267.