

# Preparation of a Multicolored Reflective Electrochromic Display Based on Monodisperse Polymeric Microspheres with N-Substituted Viologen Pendants

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**ABSTRACT:** This article describes the preparation of multicolored reflective electrochromic displays (R-ECDs) through the control of the substituents on viologen molecules. Cyanophenyl, salicylic, and alkyl groups were introduced onto 4,4'-bipyridine. The synthesized viologen moieties were reacted with methyl chloride functional groups on polymeric microspheres, which were prepared by seeded polymerization. Then, R-ECD cells were fabricated by the placement of a mixture of the viologen-modified polymeric microspheres and an electrolyte between sandwiched indium tin oxide glasses. The

R-ECDs showed an inherent white background without potential because the micrometer-range particles scattered the light, and the viologen was in a bleached state. From spectrophotometric results and visual appearances, it was confirmed that the devices showed red, green, and blue colors with respect to cyanophenyl-, salicylic-, and alkyl-substituted viologen pendants when 2.7 V was applied to the device. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 102–108, 2008

**Key words:** colloids; optics; redox polymers; surfaces

## INTRODUCTION

Viologens, which are 1,1'-disubstituted 4,4'-bipyridinium dications, are electrochromic materials of interest in various application fields, such as herbicides, photonic sensors, electron transfer devices, and anti-glare mirrors.<sup>1–5</sup> Viologens naturally stay in a dication state without an applied potential, and this results in transparency. When an appropriate potential is applied to a viologen, it is reduced to a radical cation state, showing a specific color. Because of this feature, viologens have been especially studied to realize electrochromic displays (ECDs).<sup>5–9</sup> In addition, viologens have advantages for electronic displays: a low driving voltage for visual changes, a high contrast, no need for a backlight unit like a liquid-crystal display, the possibility of a large-area display, and simple cell construction.<sup>10</sup> However, it has been reported that viologens have key weaknesses for device stability, such as electrodeposition by aging processes, dimerization, and disproportionation.<sup>11,12</sup> Also, the switching speed of a conventional solution-based ECD system depends on the diffusion of redox-active species in the electrolyte to the electrodes and is typically of the order of seconds, which is insufficient for display applications.<sup>11</sup>

Recently, an ECD based on a viologen-modified, nanoporous, nanocrystalline TiO<sub>2</sub> electrode and characterized by excellent transparency, intense blue coloration, rapid switching, and good stability has been developed.<sup>7–9,13</sup> Applying this technology, NTERA, Ltd., announced a paper-quality display technology named NanoChromics.<sup>9,14</sup> However, it has a minor disadvantage, in that an additional white reflector as a background is required to provide a reflective display for good readability like that of ink-printed paper because of the relative transparency of the nanosized TiO<sub>2</sub> particles. In our previous study,<sup>15</sup> we proposed a novel reflective electrochromic display (R-ECD) combining polymeric microspheres and viologen pendants. Because the monodisperse micrometer-range polymer particles scattered the light and the viologen on the surface of the particles was bleached without potential, the R-ECD had an inherent white background like paper. The device changed to a dark violet color at the reduction potential of the viologen pendants. In addition, the viologen molecules on the particle surface did not show any sign of side reactions for 1000 cycle tests because the viologen moieties chemically reacted through an S<sub>N</sub>2 reaction at the particle surfaces.

In this study, three kinds of viologen molecules were synthesized and applied to the viologen pendant in the R-ECD fabrication. Because the viologen could exhibit various colors depending on different substituents in the molecules,<sup>5,8,11,14</sup> various colored

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R-ECDs could be prepared. The chloro-functionalized polymeric microspheres were produced through seeded polymerization and reacted with the synthesized viologen moieties. Each color of the R-ECD prepared by polymeric microspheres having various N-substituted viologen pendants was measured with a spectrophotometer and compared visually.

## EXPERIMENTAL

### Materials

Styrene (St; Junsei, Tokyo, Japan), 1,6-hexandiol dimethacrylate (HDDM; Sartomer), and chloropropene (CP; Aldrich, Milwaukee, WI) were purified through a removal column (Aldrich) before use. 4,4'-Bipyridine, 1-chloro-2,4-dinitrobenzene, 4-aminobenzonitrile, 4-aminosalicylic acid, and 1-heptyl-4-(4-pyridyl)-pyridinium bromide were purchased from Aldrich. Poly(vinyl alcohol) (PVA; weight-average molecular weight =  $8.8 \times 10^4$  to  $9.2 \times 10^4$  g/mol, 87–89% hydrolyzed; Kuraray Co., Tokyo, Japan) and sodium lauryl sulfate (SLS; Yakuri, Osaka, Japan) were used without further purification. Ethanol (J. T. Baker, Phillipsburg, NJ), toluene (Taejung, Seoul, South Korea), and distilled and deionized water were used as received. Benzoyl peroxide (BPO; Aldrich) was recrystallized from methanol and chloroform before use.

### Synthesis of 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride<sup>8,16</sup>

4,4'-Bipyridine (1 mol) and 1-chloro-2,4-dinitrobenzene (1 mol) were refluxed in toluene for 3 days. After cooling, the precipitate was filtered and washed with ether and acetone; finally, a pale yellow powder of 1-(2,4-dinitrophenyl)-4,4'-bipyridinium chloride was produced in a yield of 80.3%. 1-(2,4-Dinitrophenyl)-4,4'-bipyridinium chloride (1 mol), dissolved in ethanol, was poured into an ethanol solution containing 4-aminosalicylic acid (1 mol), and the mixture was heated for 12 h with stirring. After cooling, 10 equiv of water was added to crystallize the byproduct, 2,4-dinitroaniline. The filtrate was mixed with chloroform, and the aqueous phase was evaporated after the removal of the chloroform phase. The residue powder was recrystallized from ethanol and washed with acetone. The final product was dried in a vacuum oven. The synthesis procedure is illustrated in Scheme 1.

### Synthesis of 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride<sup>8,16,17</sup>

1-(2,4-Dinitrophenyl)-4,4'-bipyridinium chloride (1 mol) in ethanol was added to an ethanol solution containing 4-aminobenzonitrile (1 mol) and heated for 12 h. After cooling, the byproduct in the mixture was removed by the addition of water, and the fil-

trate was evaporated and dried. The solid was recrystallized from ethanol and dried in a vacuum oven. The synthesis procedure is also exhibited in Scheme 1.

### Viologen-modified polymeric microspheres

A seeded polymerization<sup>15</sup> was carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, and a nitrogen gas inlet system to make chloro-functionalized polymeric microspheres. The polystyrene (PS) seed particles, prepared by dispersion polymerization,<sup>18</sup> were dispersed in 0.25 wt % SLS in an ethanol/water (1/5 w/w) solution by sonification and swollen with the emulsions of the second monomers (St/HDDM/CP) and BPO. The swelling was continued until all emulsions disappeared, and then the swollen particles were stabilized with a PVA aqueous solution. The polymerization was carried out at 70°C for 10 h. The chloro-functionalized particles were repeatedly washed by decantation in water and dried under the ambient temperature. Scheme 2 shows a schematic representation of the seeded polymerization.

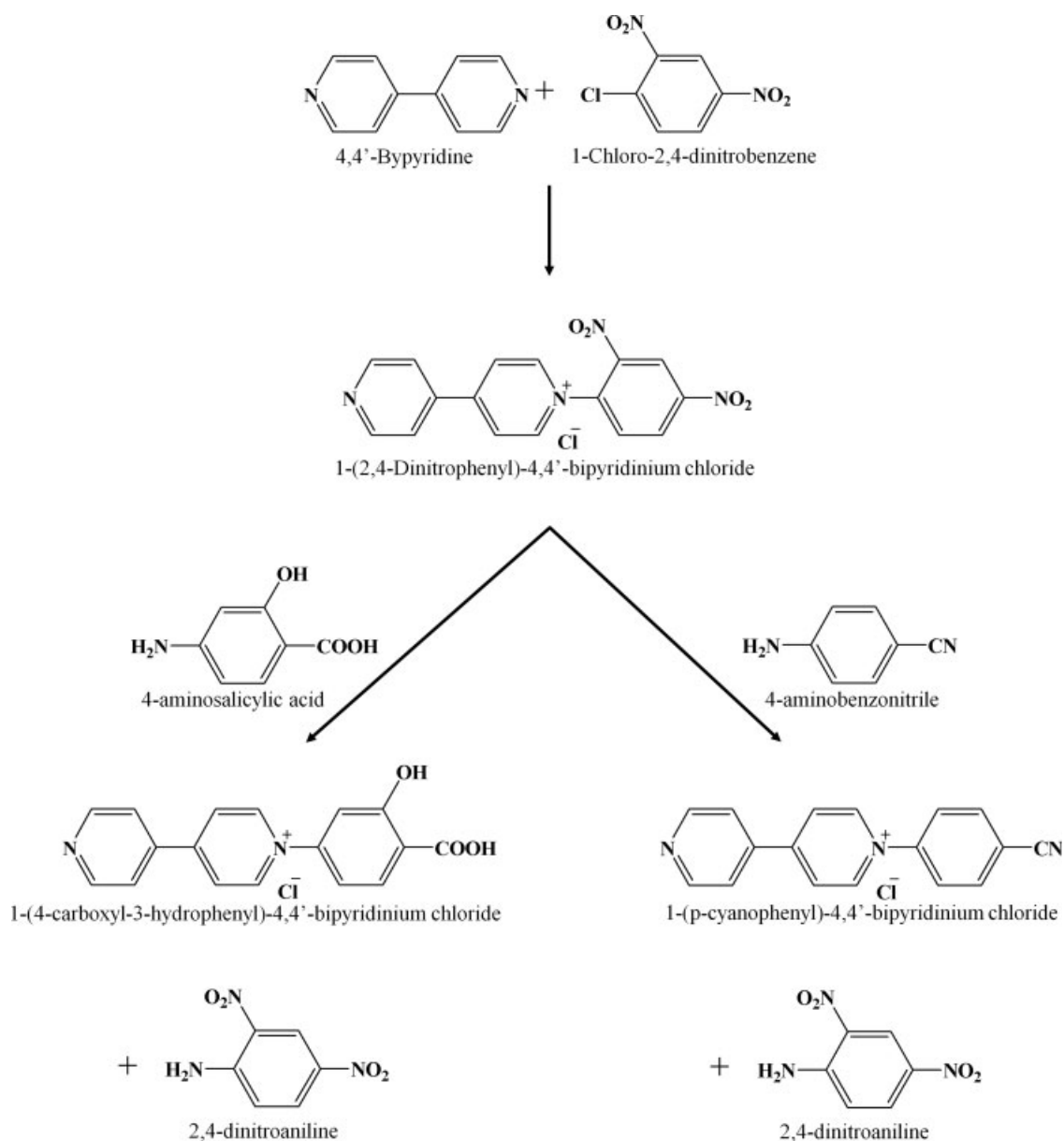
A one-necked glass flask equipped with a reflux condenser was employed for the refluxing process. Chloro-functionalized polymer particles were dispersed in toluene, and then 1-heptyl-4-(4-pyridyl)-pyridinium bromide, 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride, or 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride was added. For a good yield of the reaction between the nitrogens and methyl chloride groups, the solution was magnetically stirred throughout the refluxing. After cooling, microspheres containing viologen pendants were collected, repeatedly washed with ether and warm ethanol, and dried in a vacuum oven.

### R-ECD cell fabrication

The ECD cells consisted of two species of indium tin oxide (ITO) glasses (30 Ω; Samsung Corning, Seoul, South Korea) on which the ITO layers faced each other. The cell gap was supported by the 75-μm thickness of a poly(ethylene terephthalate) (PET) film spacer. The operational area of the cells was about  $5 \times 5$  cm<sup>2</sup>. The viologen-modified polymeric microspheres were mixed with an electrolyte supplied by Cheil Industries, Inc., (Uiwang-si, South Korea) in a weight ratio of 1/1. The mixture was rubbed onto an ITO glass and sandwiched with another piece of ITO glass, and then all edges of the cell were sealed with an insulating epoxy resin. The device fabrication process was carried out in a drybox filled with argon gas. A cross-sectional view of the R-ECD cell is shown in Scheme 3.

### Characterization

The synthesized viologen molecules were confirmed by <sup>1</sup>H-NMR spectroscopy performed in dimethyl



**Scheme 1** Synthesis routes of viologen molecules containing different substituents.

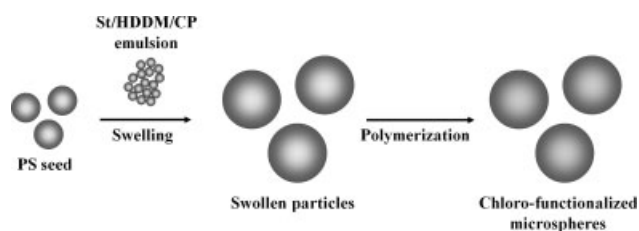
sulfoxide- $d_6$  as a solvent and tetramethylsilane (TMS) as an internal standard on a 300-MHz Varian Gemini spectrometer. The morphology of the polymer particles was monitored with an optical microscope (Microphot Fax, Nikon, Japan) and a scanning electron microscope (JSM-6300, JEOL, Tokyo, Japan). The reflectance of the ECD cells was observed with a spectrophotometer (Color-Eye 3100, Macbath, X-Rite, Inc., Grand Rapids, MI) with D65 for illumination.

## RESULTS AND DISCUSSION

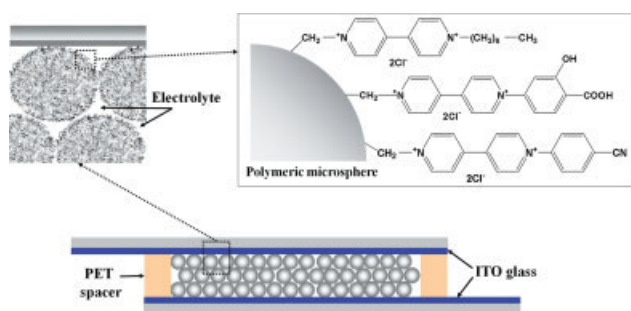
### Viologen molecules containing different substituents

Three kinds of viologen molecules were used in the preparation of the multicolored R-ECD devices. 1-

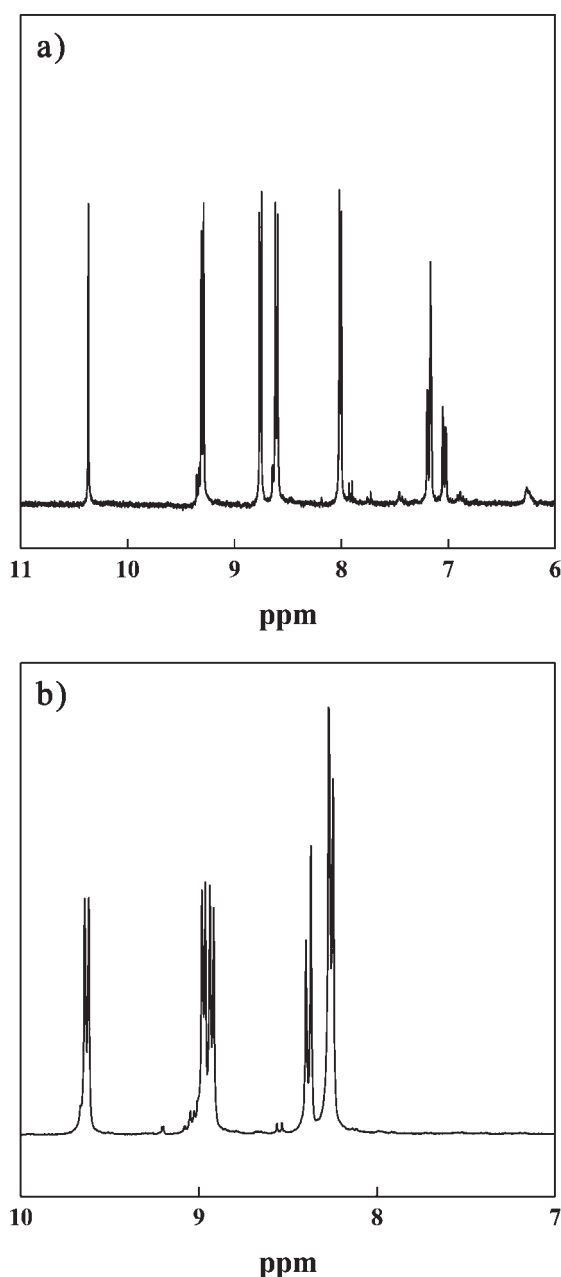
Heptyl-4-(4-pyridyl)-pyridinium bromide was used as received, and it could give a blue color. On the basis of refs. 8, 16, and 17, carboxyl hydrophenyl (salicylic acid) and cyanophenyl groups were substituted on the 4,4'-bipyridine molecule to show green and red



**Scheme 2** Schematic representation of seeded polymerization.

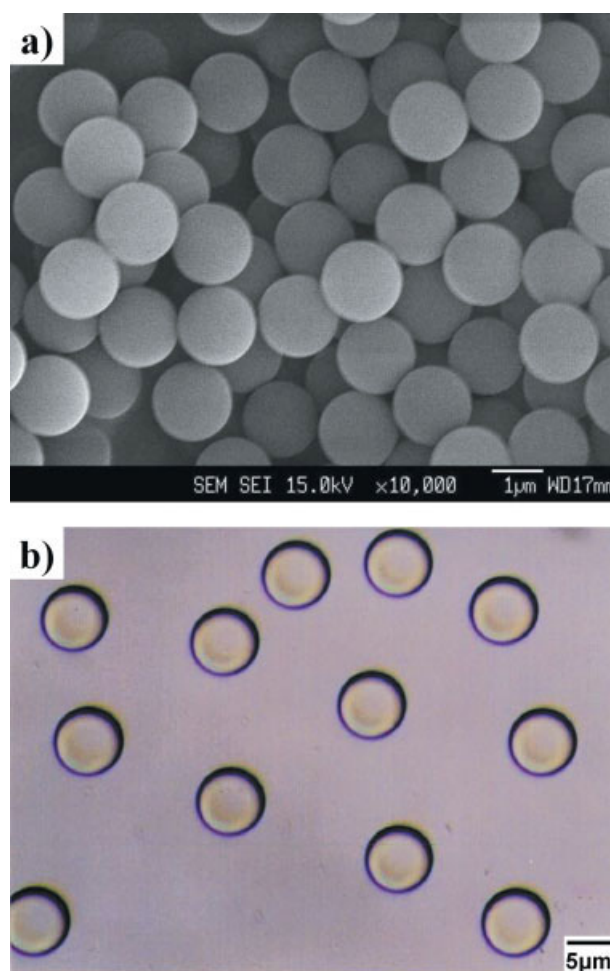


**Scheme 3** Cross-sectional view of an R-ECD cell. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

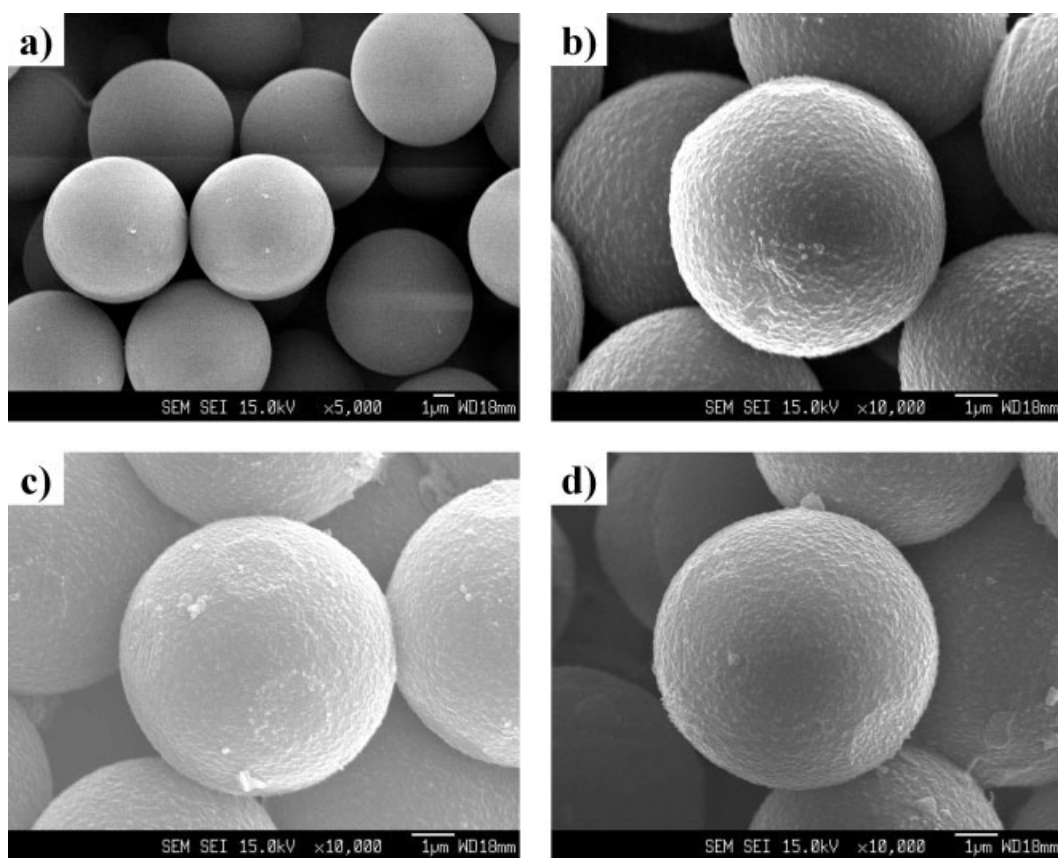


**Figure 1**  $^1\text{H-NMR}$  spectra of the synthesized viologen compounds with (a) salicylic and (b) cyanophenyl substituents.

colors, respectively. 1-Chloro-2,4-dinitrobenzene was first reacted with 4,4'-bipyridine in toluene, and then either 4-aminosalicylic acid or 4-aminobenzonitrile was reacted in the ethanol medium to induce the monoquaternized viologen moieties, as shown in Scheme 1. 2,4-Nitroaniline, a byproduct shown in the last synthesis step, was removed completely with water because it is an efficient photosensitizer interrupting the redox reaction of the viologen.<sup>11</sup> The molecular structures of the synthesized viologen moieties were ascertained from  $^1\text{H-NMR}$  spectra. In Figure 1(a), the protons in the hydroxyl and carboxyl groups of 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride appear at 6.2 and 10.3 ppm, respectively. Also, a total of 11 protons of 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride were confirmed at 7.0–7.3 (3), 8.0–8.1 (2), 8.6–8.9 (4), and 9.3–9.4 ppm (2). In the case of 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride [Fig. 1(b)], 12 protons were confirmed at 8.1–8.4 (6), 8.8–9.0 (4), and 9.5–9.7 ppm (2). The final yields of 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridi-



**Figure 2** Morphologies of (a) the PS seed particles by SEM and (b) the second-monomer-swollen PS seed particles by OM. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** SEM photographs of (a) chloro-functionalized polymeric microspheres, (b) viologen-modified polymeric microspheres containing 1-heptyl-4-(4-pyridyl)-pyridinium bromide, (c) viologen-modified polymeric microspheres containing 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride, and (d) viologen-modified polymeric microspheres containing 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride.

nium chloride and 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride were determined to be 33.1 and 29.4%, respectively. These results led to the general conclusion that viologen molecules containing different substituents were successfully synthesized.

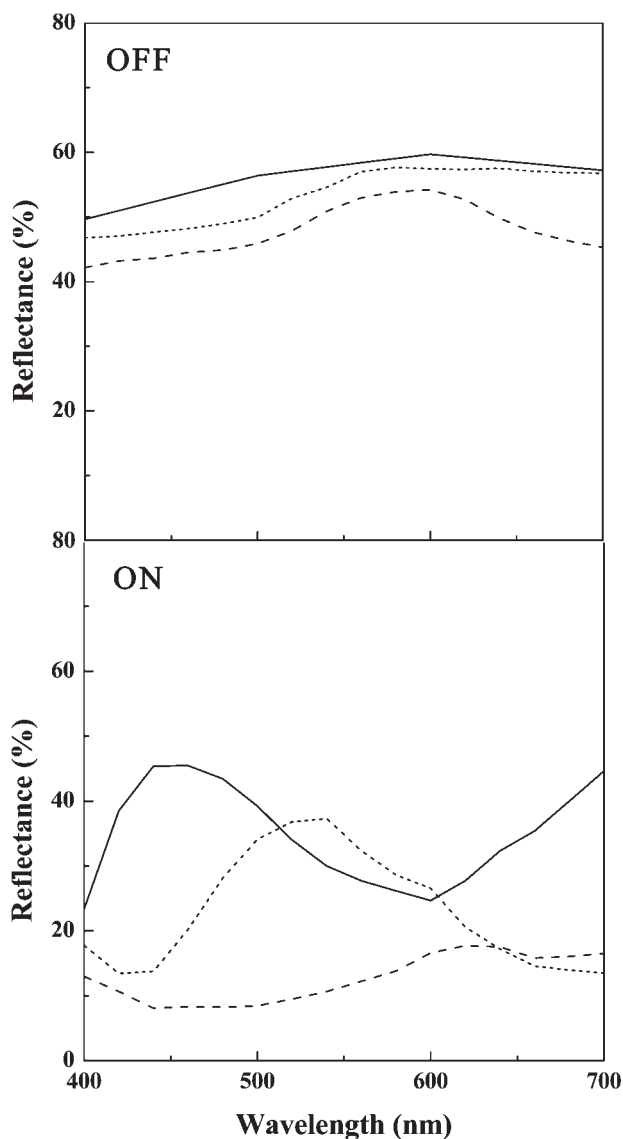
#### Viologen-modified polymeric microspheres

Figure 2(a) shows a scanning electron microscopy (SEM) image of PS particles prepared by dispersion polymerization. The PS particles, having a high monodispersity (polydispersity index = 1.01), a diameter of 1.6  $\mu\text{m}$ , and a smooth surface, were used as seed particles in the seeded polymerization procedure shown in Scheme 2. An optical microscopy (OM) image of the PS seed particles swollen by the second monomer is shown in Figure 2(b). The emulsions are not shown in the image, and the size of the swollen PS particles was uniformly increased; this indicated that the complete swelling of the second monomer into the PS seed particles was achieved. Even after the polymerization step, changes in the morphology and size of the swollen PS particles were not observed.

In the seeded polymerization, St, HDDM, and CP were chosen for the second monomer, and the

amount of the monomers was fixed at 50-fold with respect to the weight of the PS seed particles. The affinity between the PS particles and St in the second monomer could elevate the swelling of the excessive monomers into the PS seed particles efficiently, and the crosslinking structure of the polymeric microspheres could be provided by HDDM. The chloro-functional groups derived from CP existed on the surface of the polymeric microspheres because of their hydrophilic nature. When the CP content was over 30% of the second monomers, morphological changes were observed because of the difference in the interfacial tensions between the polymeric constituents.<sup>19,20</sup> Therefore, the composition ratio of the second monomers was determined to be 65/5/30 (St/HDDM/CP) by the weight percentage. In addition, an ethanol/water mixture (1/5, w/w) containing 0.25 wt % SLS was used as the medium to adjust the diffusion of the second monomers.

Figure 3(a) shows an SEM image of the chloro-functionalized polymeric microspheres. The chloro-functionalized polymeric microspheres had a smooth surface, high monodispersity, and diameter of 7.2  $\mu\text{m}$ . A rough surface was observed after the refluxing process without changes in the spherical shape



**Figure 4** Spectrophotometric analysis of an R-ECD depending on the potential: (—) 1-heptyl-4-(4-pyridyl)-pyridinium bromide, (· · ·) 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride, and (- - -) 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride.

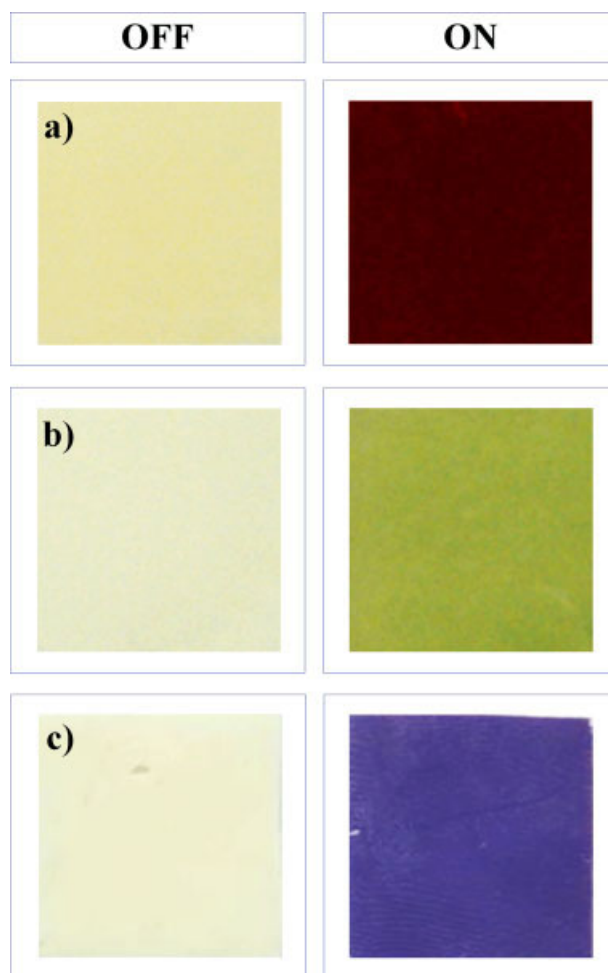
or monodispersity of the original particles, as shown in Figure 3(b–d). This trend was the same as that shown in a previous work.<sup>15</sup> The tertiary amine in each viologen molecule reacted with methyl chloride groups on the polymeric microspheres during the refluxing process. The small size of the nodules could be evaluated indirectly, and this indicated that the viologens successfully reacted with the methyl chloride groups on the surface.

#### R-ECD cells

The R-ECD cells were prepared by the placement of a mixture of the viologen-modified polymeric microspheres and an electrolyte between the ITO glasses,

as shown in Scheme 3. In the case of conventional viologen-based ECDs, the viologen molecules were dissolved in the electrolyte or deposited onto the electrode like a film. Because most ECDs are transmissive, an additional white reflector is needed to provide a reflective type display for good readability.<sup>7,9</sup> The ECD system described in this work has an inherent white background because of the close packing of the polymer particles, and the fabrication process is very simple.

Reflectance differences without and with an applied potential were achieved to investigate the optical properties of the R-ECD with respect to different substituents on the viologen molecules, as shown in Figure 4. In the off state, the visible range reflectance was over 40%. Actually, all devices showed a white color because of the micrometer-sized polymer particles and the bleached state of the viologen pendants, as shown in Figure 5. When a



**Figure 5** Photoimages of an R-ECD cell without and with potential: (a) 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride, (b) 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride, and (c) 1-heptyl-4-(4-pyridyl)-pyridinium bromide as viologen pendants. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

potential of 2.7 V was applied to the devices, the wavelengths in the range of 466.6–700.0 nm were intensely reflected, so the R-ECD showed a blue color when 1-heptyl-4-(4-pyridyl)-pyridinium bromide was used. It is generally known that the viologen containing this heptyl substituent causes a blue color.<sup>11</sup> With 1-(4-carboxy-3-hydroxyphenyl)-4,4'-bipyridinium chloride and 1-(*p*-cyanophenyl)-4,4'-bipyridinium chloride as the viologen pendants, the wavelengths of 530.0 and 620.0 nm were reflected, and this indicated that the devices showed green and red colors at a potential of 2.7 V, respectively. These results are in good agreement with the real visual appearances, as shown in Figure 5. Consequently, various colored R-ECDs could be prepared through the control of the substituents on the viologen molecules.

### CONCLUSIONS

Viologens containing different substituents were employed for multicolored R-ECD devices. Viologen molecules with cyanophenyl, salicylic, and alkyl groups as substituents were synthesized and reacted with methyl chloride groups on the surface of microspheres. The R-ECD cells were fabricated through the mixing of the viologen-modified polymeric microspheres and an electrolyte. Comparing spectrophotometric and visual appearance results, we confirmed that each R-ECD cell exhibited red, green, and blue colors within the potential when cyanophenyl, salicylic, and alkyl substituents were used on the viologen molecules, respectively. Various col-

ored R-ECDs were successfully achieved by the modification of the viologen molecules.

### References

1. Schmalzl, K. J.; Summers, L. A. *Aust J Chem* 1977, 30, 657.
2. Lahav, M.; Ranjit, K. T.; Katz, E.; Willner, I. *Chem Commun* 1997, 3, 259.
3. Poulos, A. T.; Kelley, C. K.; SImone, R. *J Phys Chem* 1981, 85, 823.
4. Rosseinsky, D. R.; Mortimer, R. J. *Adv Mater* 2001, 13, 783.
5. Michaelis, A.; Berneth, H.; Haaer, D.; Kostromine, S.; Neigl, R.; Schmidt, R. *Adv Mater* 2001, 13, 1825.
6. Yasuda, A.; Seto, J. *J Electroanal Chem* 1990, 283, 197.
7. Bonhôte, P.; Gogniat, E.; Campus, F.; Walder, L.; Grätzel, M. *Displays* 1999, 20, 137.
8. Cinnsealach, R.; Boschloo, G.; Rao, S. N.; Fitzmaurice, D. *Sol Energ Mater Sol Cells* 1999, 57, 107.
9. Bach, U.; Corr, D.; Lupo, D.; Pichot, F.; Ryan, M. *Adv Mater* 2002, 14, 845.
10. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, 1995.
11. Monk, P. M. S. *The Viologens*; Wiley: Chichester, England, 1998.
12. Monk, P. M. S. *J Electroanal Chem* 1997, 432, 175.
13. Felderhoff, M.; Heinen, S.; Molisho, N.; Webersinn, S.; Walder, L. *Helv Chim Acta* 2000, 83, 181.
14. Corr, D.; Bach, U.; Fay, D.; Kinsella, M.; McAtamney, C.; O'Reilly, F.; Rao, S. N.; Stobie, N. *Solid State Ionics* 2003, 165, 315.
15. Ryu, J.-H.; Shin, D.-O.; Suh, K.-D. *J Polym Sci Part A: Polym Chem* 2005, 43, 6562.
16. Allen, J. G. *Brit. Pat.* 1,399,595 (1975).
17. Park, K.; Lee, J.; Han, D. *Bull Korean Chem Soc* 1985, 6, 141.
18. Ryu, J.-H.; Kim, J.-W.; Suh, K.-D. *Colloid Polym Sci* 1999, 277, 1205.
19. Park, J.-G.; Kim, J.-W.; Suh, K.-D. *Colloid Polym Sci* 2001, 279, 638.
20. Sundberg, D. C.; Casassa, A. P.; Pantazopoulos, J.; Muscato, M. R. *J Appl Polym Sci* 1990, 41, 1425.