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INVITED PAPER *Special Section on Electronic Displays*

Novel Electrochromic Polymer for Electronic Paper

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SUMMARY Electrochromic (EC) type e-paper is attracted with colorfulness and clearness. We have been researching and developing the material for EC type e-paper. We developed novel EC Polymers for e-paper. Our EC polymers are kinds of conductive polymers (CP). CP has some characteristics. One is electrochromism, and the other is electrochemical polymerization. Electrochromism of CP has a good memory effect. And electrochemical polymerization is suitable for printable electronics, for instance, ink-jet, screen print, and so on. Our EC polymers are comprised with thiophene derivatives and pi-conjugated X unit. To our knowledge, this thiophene derivatives are novel structure for EC polymers. These EC polymers have the electrochromic characteristic which change from coloration state to clear state. And we can adjust the color which we want by changing only X unit. And we made segment matrix EC display with our EC polymers by ink-jet printing. Our EC polymers are suitable for printable electronics, flexible substrate, and roll-to-roll process. We introduce our developing technologies.

key words: *electronic paper, electrochromic polymer, printable electronics, conductive polymer*

1. Introduction

E-paper is an area great interest for electronics, because it can be substituted for printed papers, which enable a better life for human being by solving the problems concerning environmental issues such as exhaustion of natural resources due to the paper productions. In addition, the flexible and reflective characteristics of the device can open up new concept applications [1].

Various techniques have been tried to realize the practical usage of E-paper, such as electrophoresis type [2], electro-wetting type [3], microelectromechanical mirror type [4], reflective liquid crystal type and electrochromic type [5].

Electrochromic(EC) type has various advantages such as low voltage, high reflectance and the freedom of structure designs, for example, parallel or stack structure. And then, there are some kinds of EC materials, which are inorganic (metal oxide) type for example WO3 [6], organic molecular type for example Viologen [7], polymer type for example conductive polymer (CP) [8], and organic/inorganic hybrid type [9]. Table 1 is summarized above EC materials.

Table 1 Summary of EC materials.

Inorganic		organic	
Metal oxide	Hybrid	Low molecule	Polymer
ex.)WO3	ex.) complex of metal ions with organic ligands	ex.) Viologen	ex.)Conductive polymer

2. Features of Polymer Type (Electrochromism and Electropolymerization)

CP has some features. One is electrochromism. Figure 1 shows the principle of polymer electrochromism. CP can be two states those are doping state and de-doping state. Doping state is called quinoidal structure, meanwhile de-dopoing state is called aromatic structure. Usually, de-doping state of CP is insulate and has absorption band in visible area. This absorption band is derived from band gap energy. When CP is applied voltage, CP donates (or accepts) electron and is transformed to quinoidal structure. Quinoidal structure is conductive. Because of keeping electronic neutral state in system, anion or cation (dopant, usually electrolyte) is needed. Doping and de-doping states can switch reversibly each other with applied voltage. And these states are bistable with open-circuit.

Band gap energy of quinoidal structure is smaller than that of normal CP (aromatic structure). When band gap energy is enough small, absorption band is shifted to Near-Infrared area and there is no absorption band in visible area (see Fig. 1).

At this time, human eyes can't recognize coloration. Namely, CP has coloration in aromatic structure (de-doping state), otherwise CP is transparent in quinoidal structure (doping state). We can control this switching with applied voltage.

And coloration of CP depends on de-doping level. In other words, full de-doping state has deep color, meanwhile half de-doping state has shallow color. And we can control de-doping level with the strength of voltage. Namely, color gradation can be controlled with applied voltage.

Another feature is electrochemical polymerization. Monomer of CP is polymerized with electrochemical polymerization that occurs on the electrode. For example, in e-paper, the electrode corresponds to ITO. Figure 2 shows

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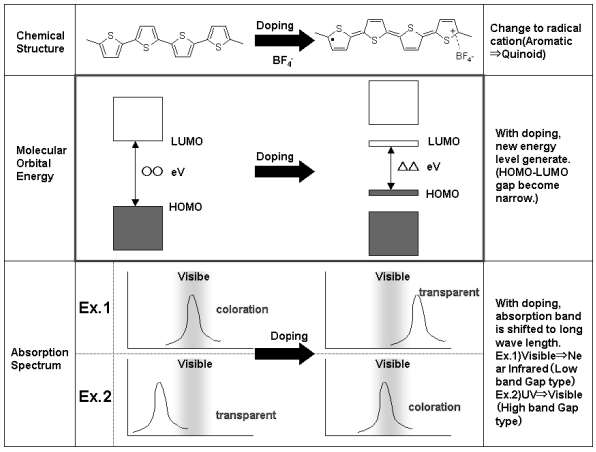


Fig. 1 Principle of polymer electrochromism.

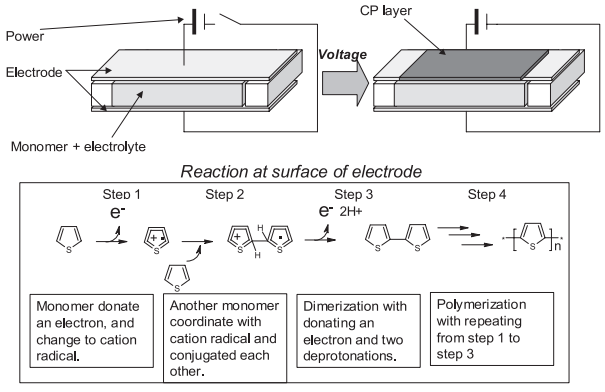


Fig. 2 Mechanism of CP's polymerization on electrode.

mechanism of CP's polymerization on the electrode.

In Fig. 2, for the explanation of mechanism, I picked up thiophene as representative. Firstly, a monomer donates an electron to the electrode, and become to the cation radical. (step 1) Next, another monomer coordinates with the cation radical. And then they conjugated each other. (step 2) Next, Dimerization happens with pulling an electron by electrode and two deprotonation. (step 3) So polymerization occurs with repeating from step 1 to step 3.

Because this polymerization needs the electron donation toward electrode, it happens only on the electrode. Once monomers grow up to be the CP, CP can't be dissolved to any solution (Monomer of CP can be dissolved to variable solutions.). So CP are piled up onto the electrode. We thought of making good use of this electropolymerization as sedimentary EC layer on the ITO.

In this way, CP has some unique features. So we are developing polymer type material.

3. Manufacturing Process of EC Polymer Type E-Paper

Electrochemical polymerization is easy way, because the solution of conductive monomer dissolved in electrolyte

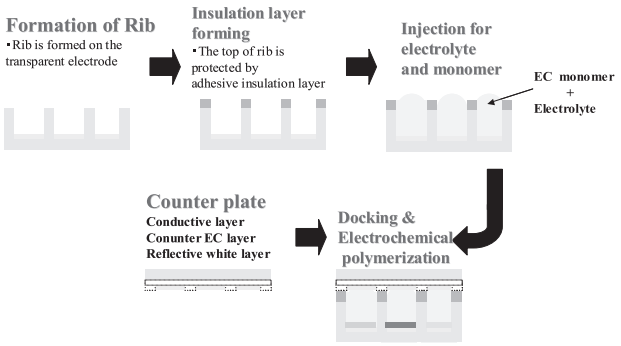


Fig. 3 Manufacturing process for EC polymer type e-paper.

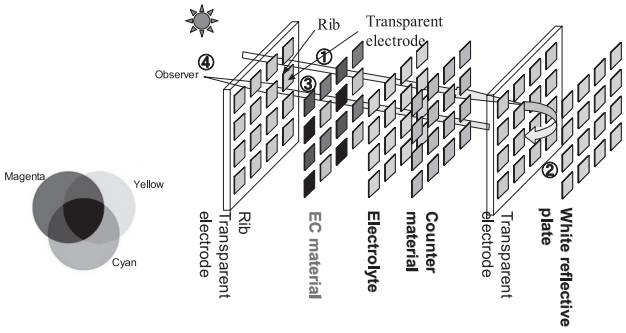


Fig. 4 The structure of EC display.

is printed on electrode, and then sandwiched with counter electrode, then electrochemical polymerized, and then CP film can be used for EC layer. Figure 3 shows the manufacturing process for EC polymer type e-paper. Figure 4 shows the structure of EC display.

Our CP is good EC material suited for manufacturing of e-paper. First, incident light go through EC layer, and are reflected at the white reflection plate, and go through EC layer again, finally, observer can see some colorations. When EC layer has some coloration, observer can see some color, for example cyan, magenta, yellow, and so on. When EC layer is transparent, observer can see white color. EC layer can be applied for both a juxtaposition mixture method and a lamination mixture method.

4. Our Novel EC Polymer

We have developed novel EC polymers that each color changes from Cyan, Magenta, and Yellow to transparent. Our EC polymers are thiophene derivatives. Figure 5 shows the preparation scheme of our EC polymer.

These EC polymers have intramolecular hydrogen bond, so have high planer polymer backbone. The EC monomers of our polymers have good solubility into various solutions with electrolyte. And the solution containing the monomer and electrolyte is suitable for printed electronics, because the liquid properties which are important for printing can be adjusted easily.

The color of Cyan, Magenta, and Yellow can be adjusted by changing X unit. The X unit is preferable to be

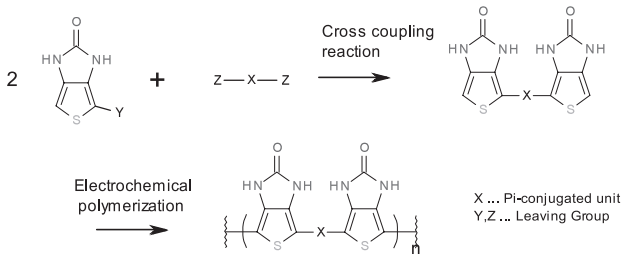


Fig. 5 The preparation scheme of our EC polymer.

pi-conjugated structure. For example, benzene, carbazole, and thiophene should be suitable. And color changes of these polymers are observed between coloration and pale gray. These EC polymers can be driven at low voltage (+1.5∼−0.5 V vs. Ag/AgCl reference). The response time of these EC polymers are approximately 500 ms. We have confirmed that we could control gradations with 4 stages at least.

Figure 6 shows the UV-Vis spectra of each EC polymers, (a) Cyan, (b) Magenta, and (c) Yellow. These UV-Vis spectra were measured in each color states according to applied volatages (+1.4 V to −0.5 V vs Ag/AgCl reference). Figure 7 shows color image on CIExy 1931.

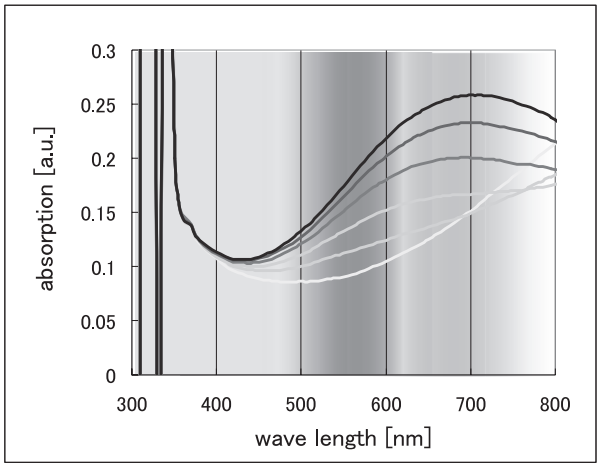
5. Segment Matrix E-Paper Made with Printed Electronics

We used these EC polymers (monomer) for printed electronics. We made the solution of EC monomer and printed on demand with ink-jet printing. We introduce the printable procedure blow.

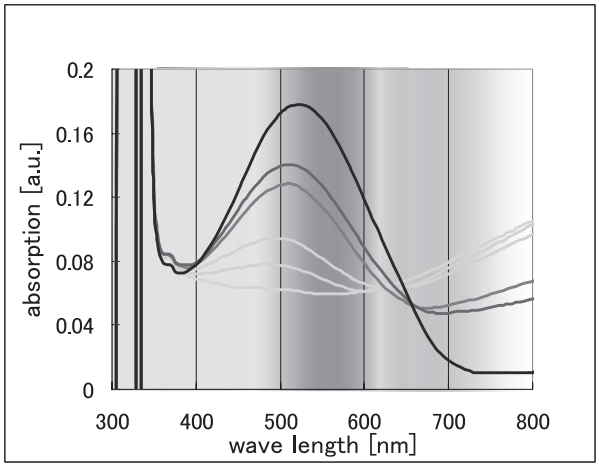
1. Preparation of rib (50×50 μm/one dot) which is formed by photolithography on ITO glass electrode
2. Preparation of solution containing EC monomer and electrolyte
3. Ink-jet printing in ribs on demand
4. Glued with another ITO glass electrode
5. Apply + 1.5 V voltage on rib ITO
6. Switch applied voltage (−1.5 V), EC polymer changes the state between coloration and transparent

Figure 8 shows the image of ink-jet printing.
Figure 9 shows the image of rib on ITO glass.
Figure 10 shows the image of enlarged image of ECD.
Figure 11 shows the image of ECD.

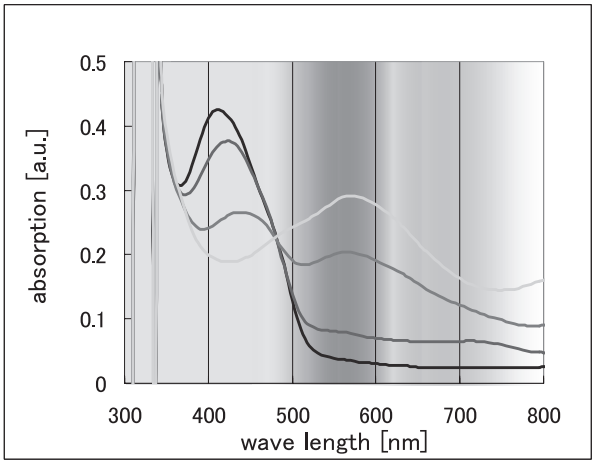
Electrochromic Display (ECD) in Figs. 10 and 11 are mono-color segment matrix. ECD in Figs. 10 and 11 are consisted of two 5 × 5 cm ITO glass electrodes and rib. The character on these segment matrices display can switch between appearing and disappearing. Rib which is formed by photolithography on ITO glass electrode is separating adjacent pixels (see Fig. 9). Because our solution containing EC monomer and electrolyte was suitable for ink-jet printing, we could confirm that liquid pillar went straight forward substrate (see Fig. 8).



(a) Cyan



(b) Magenta



(c) yellow

Fig. 6 UV-Vis spectra of each color (a) Cyan, (b) Magenta, and (c) Yellow.

6. Conclusion

In this paper, our novel EC polymer and EC type segment matrix e-paper is introduced.

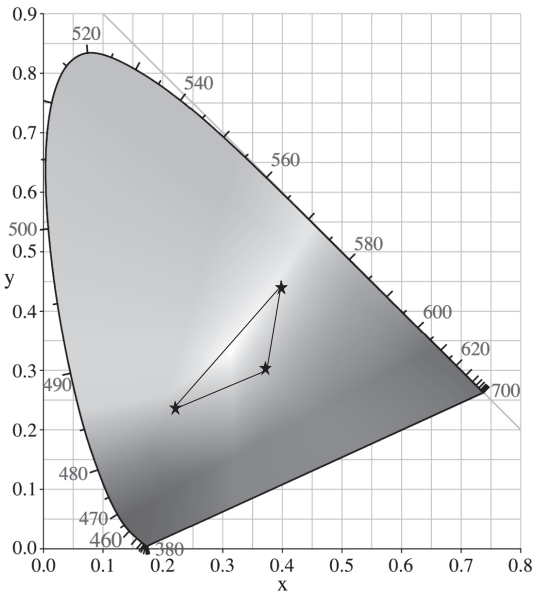


Fig. 7 Color image on CIExy 1931.

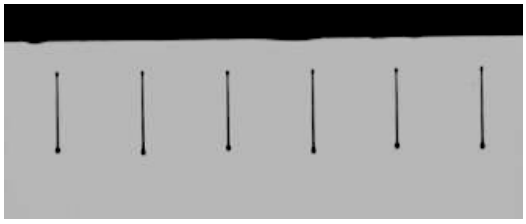


Fig. 8 The image of ink-jet printing.

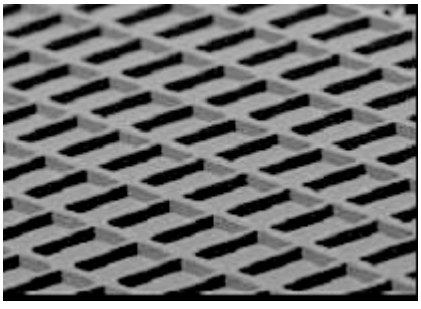


Fig. 9 The image of rib on ITO glass.

CP has some features. One is electrochromism, and another is electrochemical polymerization. These features are suitable for printed electronics. We have developed novel EC polymer that color change from Cyan, Magenta, and Yellow to pale gray. And we made ECD with our EC polymer. The summary of Kuraray EC polymer type e-paper is below.

Material

* Freedom of color control
  ex1.) controllable with co-polymarization
  ex.2) gradation control
* Low voltage

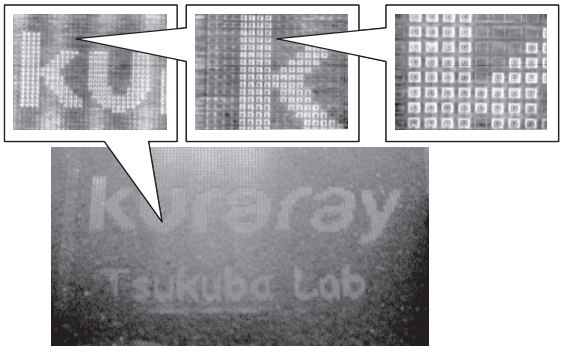


Fig. 10 The image of enlarged image of ECD.

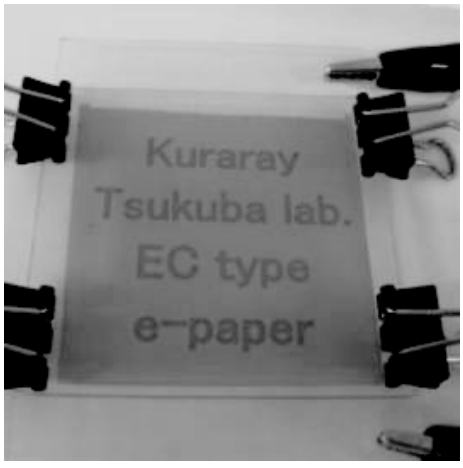


Fig. 11 The image of ECD.

ex.) enable to drive between +3 and −3 V

Manufacturing process

* Suitable for printable process
  ex.) ink-jet printing,screen printing, and so on
* Suitable for flexible e-paper
  ex.) Roll to Roll process

But there are still some problems. We will make an effort to look for solutions. First, we have to make the contrast between coloration and transparent higher. Second, we have to improve the performance of mixed color. Third, we have to control the cross-talk problem in passive-matrix driving. Now we are developing for passive-matrix e-paper which using these EC polymers.

Finally, our EC polymers are suitable for not only reflective type display but also see-through type display. We are seeking for new application too.

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