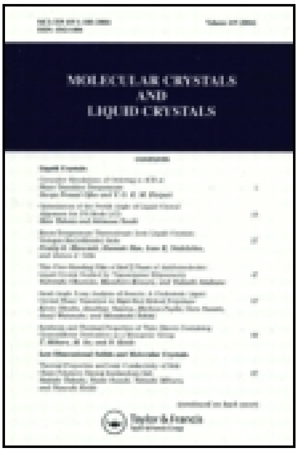

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High Contrast and Dynamic Electrochromic Display with Thin Solid Hyper-Branched Polymer Film

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High Contrast and Dynamic Electrochromic Display with Thin Solid Hyper-Branched Polymer Film

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A new hyperbranched electrochromic (EC) polymer containing many viologen units was developed. The EC polymer film was easily fabricated by a spin coating method and employed as thin EC display film. All-solid EC display was constructed with polymeric electrolyte gel and hyperbranched polymer. The EC display was operated with good contrast and rapid response at low bias voltage, 2.5 V.

Keywords Electrochromism; hyperbranched polymer; viologen

Introduction

Electrochromic (EC) displays have received much attention because of a brilliant color and low power consumption [1–5]. Electrochromism is defined as a color change by oxidation or reduction when an appropriate electric potential is applied. Viologen, one of typical organic EC materials, has been consistently studied due to its outstanding EC properties and a good environmental stability under appropriate conditions. Early application of viologen was made in aqueous electrolyte display system [3]. However, leakage of solution is a serious problem to practical applications. There have been a lot of efforts to immobilize viologen on electrode surfaces by polymerization [4] and by adsorption or chemical modification of an inorganic material as hybrid system [5]. Although thin film type EC devices have advantages for applications, there is usually trade-off between their response time and the contrast.

In the present paper, we tried to solve the problem by using hyperbranched polymers containing EC units at high concentrations. Hyperbranched polymers usually show superior properties such as better solubility and lower viscosity than linear ones with similar molecular weight. We developed a new hyperbranched EC polymer

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(HBP-EC) containing many viologen units, and studied the EC properties of all-solid device fabricated from HBP.

Experimental

Synthesis of Monomer

Under nitrogen atmosphere, 4.6 g (30 mmol) of chloromethylstyrene and 0.78 g (5 mmol) of 4,4′-bipyridine were dissolved in a 150 ml of N,N-dimethylformamide and stirred at 60°C for 20 h. After cooling to room temperature, the precipitate was filtrated and the filtrate was washed with acetone. The product was dried to yield 2 g of bis(4-vinylbenzyl)-4, 4′-bipyridinium dichlorides as yellow powder (50%).

Polymerization

Under nitrogen atmosphere, 1.15 g (2.5 mmol) of bis(4-vinylbenzyl)-4, 4′-bipyridinium and 1.15 g (5 mmol) of dimethyl 2,2′-azobisisobutyrate (MAIB) were dissolved in 44 g of ethyleneglycol and stirred at 100°C for 6 h. After reaction, the mixture solution was concentrated by evaporation. The product was dissolved in 5 mL methanol and reprecipitated by pouring into 400 mL ethylacetate. The precipitate was filtered and dried to yield 1.5 g (65%) of HBP-EC as pale pink powder.

Fabrication of EC Device

The EC device is composed of an electrochromic layer (ECL) and a charge transport layer (CTL) between two transparent ITO electrode substrates as shown in Figure 1. The ECL film was fabricated by spin coating 2 wt% methanol solution of HBP-EC onto the ITO electrode. The EC film was dried for 1 day on a hotplate at 40°C. The ECL thickness was estimated as 200 nm by a KEYECE laser microscope and by atomic force microscopy (AFM) with a SPI3800 N Probe station. Polymer electrolyte gel as CTL was prepared from a mixture of lithium perchlorate, poly(methylmethacrylate), propylene carbonate and acetonitrile [6,7]. This electrolyte gel was sandwiched between the ECL-coated ITO and bare ITO electrodes, which dried for 1 day on a hotplate at 40°C in ambient atmosphere. The thickness of CTL was estimated to be about 15 μm by a micrometer.

Characterization

The ^{1}H NMR spectra were measured with Bruker AVANCE-500-K-S (500 MHz). Gel permeation chromatography (GPC) was performed at 40°C, using a Tosoh

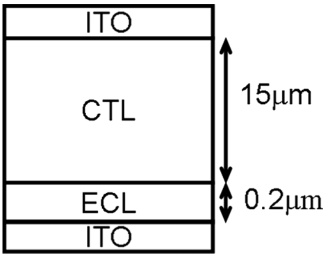

Figure 1. Structure of EC device.

HLC-8220 GPC chromatograph (columns; G6000PWXL-CP and G3000PWXL-CP with 20 mM of aqueous solutions of sodium nitrate as an eluent). From the GPC results, number average (Mn) and weight-average (Mw) molecular weights were estimated with calibrations by the poly(ethyleneglycol) standard. UV-visible spectra of the solution were measured by Hitachi U-4100. Cyclic voltammogram (CV) was observed by Autolab PGSTA128 N. Under applied bias voltage, absorption spectra were measured with an Ocean Optics USB 4000 fiber-optic spectrophotometer equipped with a Xenon lamp (Hamamatsu C7535) as a light source.

Results and Discussion

With a new class of radical polymerization termed as initiator-fragment incorporated radical polymerization (IFIRP), a new hyper-branched EC polymer (HBP-EC) containing high density of viologens was obtained. The weight-average (Mw) molecular weight was estimated for 1,300,000 by the poly(ethyleneglycol) standard. The molecular structure is shown in Figure 2. This polymer is well dissolved in polar solvents such as water and methanol. Solubility of HBP-EC can be easily controlled by counter anions. Exchange of counter anions from choloride (Cl^-) to hexafluorophosphate (PF_6^-) makes HBP-EC insoluble in polar solvents. Good solubility and solvent selectivity are very advantageous to EC device fabrication as mentioned below.

UV-visible absorption spectra of HBP-EC were measured in aqueous solutions before and after adding a chemical reducing agent, $Na_2S_2O_4$. Before reduction of HBP-EC, there was no absorption peak in the visible region. Upon addition of $Na_2S_2O_4$, there appeared a new absorption with three peaks at 380 nm, 530 nm and 900 nm as shown in Figure 3. Viologen radical cations formed by one electron reduction of viologens are known to show absorption peaks at 400 and 605 nm

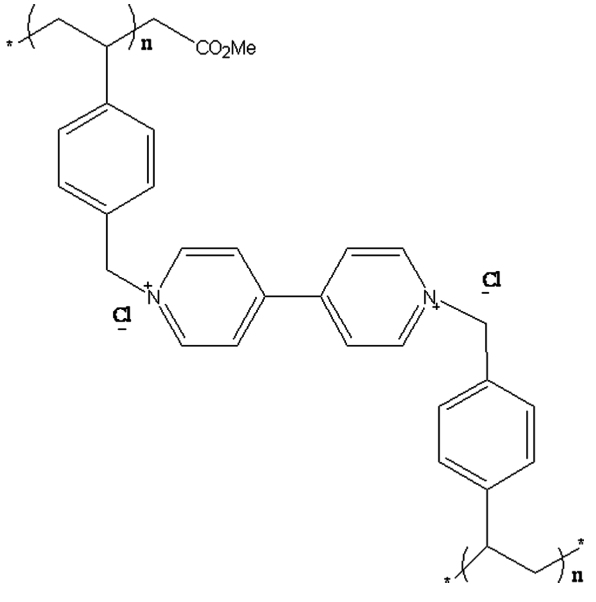

Figure 2. Molecular structure of HBP-EC.

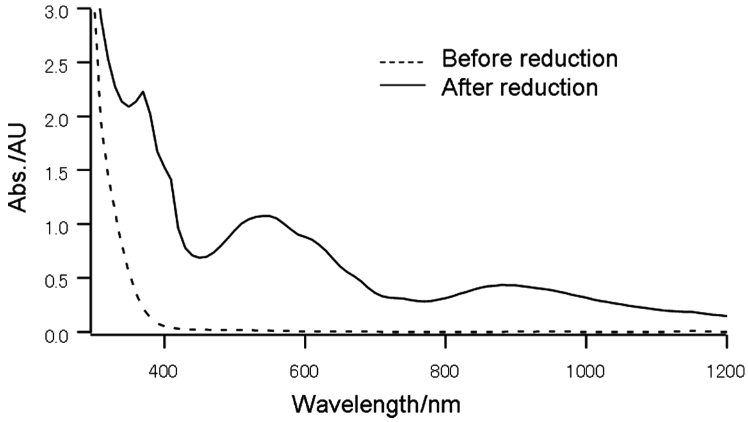

Figure 3. UV-visible absorption spectra of HBP-EC aqueous solutions (1 mM) before and after adding chemical reducing agent, $Na_2S_2O_4$.

due to the short and long axis transitions, respectively [8]. Blue-shifted absorption peaks at 380 nm and 530 nm observed in the present system were most probably assigned to the short and long axis transitions of viologen radical cation dimers, respectively. Viologen radical cation molecules existed very close to each other in the hyperbranched polymer are presumed to result in interactions of transition dipole moments between adjacent radical cations in a similar manner as H-aggregates [9]. The absorption peak observed at 900 nm was assigned to the charge transfer (CT) interaction between neighboring radical cationic viologen units [10].

All-solid state EC display consisting of ECL and CTL between two ITO electrodes was prepared. ECL and CTL were fabricated from solutions with different solvents as mentioned above. Since HBP-EC is soluble in neither propylene carbonate nor acetonitrile, The EC device was easily prepared with the ECL and CTL solid films overlapped.

Electrochemical property of HBP-EC was investigated by cyclic voltammetry (CV). With the propylene carbonate solution containing 0.1 M of $LiClO_4$ as a supporting electrolyte, CV measurement of HBP-EC was made in the range of -1.5 V $\sim$0 V vs. Ag/Ag^+ at a scan rate of 100 mV/s with three electrodes consisting of glassy carbon working electrode, platinum counter electrode and Ag/Ag^+ reference electrode. Differential pulse voltammetry was also measured at 20 mV/s. As shown in Figure 4, there were two redox peaks corresponding to the first and second redox reactions of viologen. The first redox peak at -0.65 V is assigned to the change of radical cationic state ($V^{+}\cdot$) from dicationic state (V^{2+}). The second redox peak observed at -1.1 V was attributed to the doubly reduced state ($V^{2}\cdot$).

When the ITO electrode contacting to ECL is negatively biased by an external voltage at -2.5 V, the transparent EC cell rapidly turned to magenta color as shown in Figure 5. By an application of reverse bias voltage, the EC cell was rapidly bleached. The absorbance at 530 nm was plotted as a function of time during the change of an applied voltage in Figure 6. The reversible coloring and bleaching behavior was observed repeatedly. The absorbance at 530 nm was 0.02 with -2 V bias and 0.15 with -2.5 V bias, respectively. The response times were 5 and 2 seconds

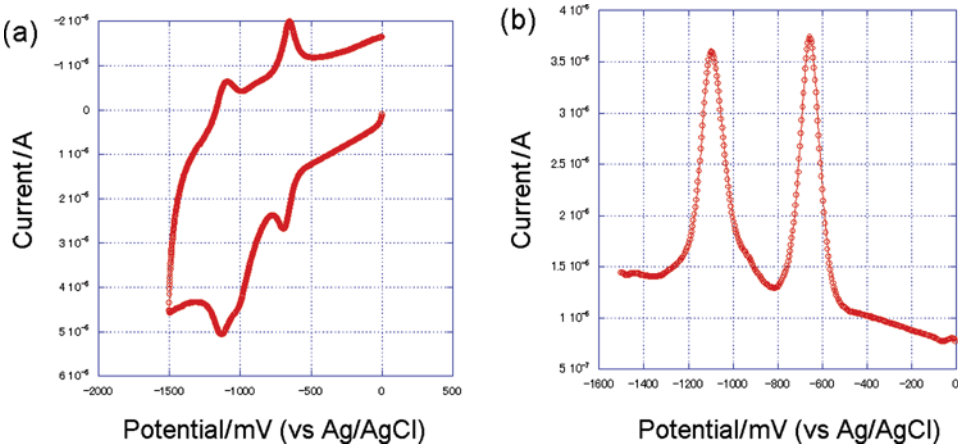

Figure 4. (a) CV curves of HBP-EC with scan rate at 100 mV/s in the range of −1.1 V to 0.75 V vs Ag/Ag^+. (b) Differential pulse voltammetry at 20 mV/s.

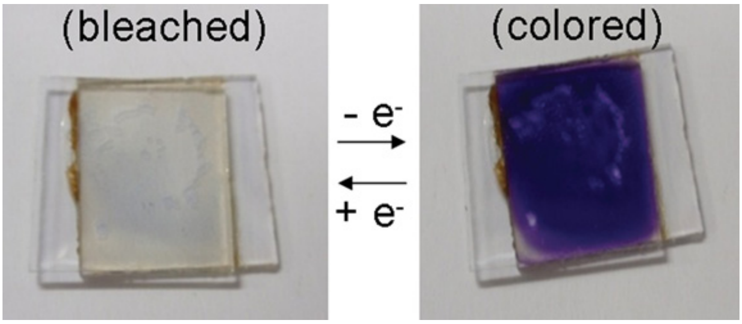

Figure 5. Color change of EC cell by bias voltages of ±2.5 V.

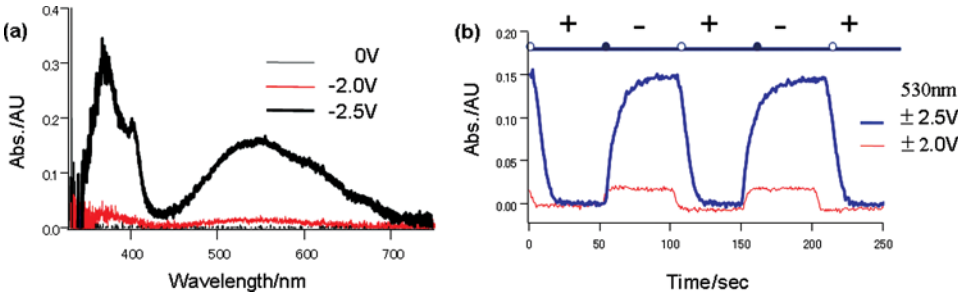

Figure 6. (a) Absorption spectra of HBP-EC for the electrical voltage of 0, −2, −2.5 V, (b) reversible changes of absorbance at 530 nm during repeated applications of bias voltage −2 V/+2 V and −2.5 V/+2.5 V, respectively.

for coloring and bleaching, respectively. This high speed response and low applied voltage is attributed to the fabrication of the thin ECL film containing high density of chromophores. The response time and display contrast can be controlled by voltage and/or thickness of ECL. Furthermore, there is no need to apply a voltage except a writing or erasing process so that the EC display can be operated with a very low-power consumption.

Conclusion

We developed a new hyperbranched EC polymer and fabricated the EC device consisting of thin solid films of ECL and CTL. By using a hyperbranched polymer, the EC solid film was easily fabricated by spin-coating. The EC display with good contrast and fast response at a low bias voltage was achieved by the very thin EC films containing high concentrations of chromophores.

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