



Feature article

Recent advances in electrochromic polymers

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ABSTRACT

Electrochromic polymers are attractive materials with enormous potential in the rapidly developing area of plastic electronics due to their flexibility, low-power consumption, ease of processing and low processing cost. Electrochromic devices created with electrochromic polymers are likely to be alternatives or supplements to the conventional inorganic electrochromic devices, which face challenges of durability and electrochromic properties. Several novel electrochromic polyimides, polyamides, and polynorbornenes prepared via polycondensation, ring-opening metathesis polymerisation (ROMP), etc., are introduced in this article. These various polymer species exhibit high thermal stability and mechanical strength.

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1. Introduction

At present, electrochromic (EC) polymers have attained prominence due to their low cost, easy processing, easy control of perceived colour and other properties by blending, lamination, patterning and copolymerisation techniques [1,2]. EC polymers have long lifetimes for use, high optical contrast [1,2], stable oxidation states, excellent switching reproducibility [3], and flexibility, so they can be applied to areas that are uneven or foldable [4] compared to their inorganic and small organic counterparts. More importantly, many polymers can exhibit more than two reduction-oxidation (redox) states and generate multiple colours [5].

In view of these advantages, EC polymers are expected to find widespread application in thin film transistors, displays (OLED), optical shutters (smart windows, mirrors, sunglasses), cathode ray tubes with variable transmittance, thermal-exposure indicators for frozen foods, EC printing, light intensity controllers, stealth coating [6], electric activity of the cell membrane [7], resolving the respective influence of electron and proton transfer processes in bacterial reactions [8], probing local potentials on surfaces of biological cell membranes [9] and smart papers [1]. Proposed applications include camouflage materials, spacecraft thermal control,

and controllable light-reflective or light-transmissive display devices for optical information and storage [1].

The properties, synthesis and application of EC polymers have been reviewed in many papers. Roncali [10] has reviewed poly(thiophenes), Mortimer et al. [1] have reviewed poly(thiophenes), poly(pyrroles), and poly(anilines), and Reynolds [11] has reviewed π -conjugated polymers (CPs), colour control, etc. Based on these reviews, there is a huge interest in these polymeric materials as a response to the development and demand of the new electrochromic device (ECD) concepts. However, until now, the commercialisation of these polymers is still in progress because of their complicated synthesis process, low thermal stability, and lack of mechanical properties.

Polyimide (PI), polyamide (PA) and polynorbornene (PNB) have high thermal stability and good mechanical properties. The polymerisation of PIs and PAs is very easy and cheap. Kapton[®] (PI) and Kevlar[®] (PA) are the most popular products among the polymerised PIs and PAs. Meanwhile, Zeonex[®] (Nippon Zeon) and Arton[®] (JSR), two PNBs, have high transparency and are used in optical applications. These commercialised high performance polymeric materials may have tremendous potential for application in the ECDs if they contain electroactive chromophore(s). These EC polymers have fast response times, and their electroactivity can last for numerous cycles.

In this article, we will introduce some PIs, PAs, and PNBs containing electroactive chromophores with high thermal stability and mechanical properties to be applied as EC materials. All of these electrochromic polymers remain in the solid state at all times

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Abbreviations/Glossary

ACN	Acetonitrile
Aramid	aromatic polyamide
CB	chlorobenzene
CP	conjugated polymer
CTE	thermal expansion coefficient
CV	cyclic voltammetry
DCM	dichloromethane
DMAc	N,N-dimethylacetamide
DMF	dimethylformamide
EC	electrochromic
ECD	electrochromic device
HOMO	highest occupied molecular orbital
ITO	indium tin oxide
LB	Langmuir–Blodgett
LUMO	lowest unoccupied molecular orbital
LOIs	limiting oxygen indices

m-Cresol	meta-cresol
NIR	near-infrared
NMP	N-methyl-2-pyrrolidone
NN	nitronyl nitroxide
OLED	organic light-emitting diode
PI	polyimide
PNB	polynorbornene
ProDOT	3,4-(propane-1,3-diyldioxy)thiophene
ProDOT-Me2	dimethyl-3,4-(propane-1,3-diyldioxy)thiophene
Redox	reduction-oxidation
ROMP	ring-opening metathesis polymerisation
SOMO	single occupied molecular orbital
TBAP	tetrabutylammonium perchlorate
T_{dx}	decomposition temperature for $x\%$ loss
T_g	glass-transition temperatures
THF	tetrahydrofuran
TPA	triphenylamine

during EC usage. Electrochromic polymers have the potential for use in the all-solid-state ECD.

2. Polyimides (PIs)

PIs are attractive electrochromic polymers due to their unique mechanical properties, thermal stability, and morphological properties. PIs rank among the most heat-resistant polymers and are widely used in adhesives, dielectrics, photoresistors, nonlinear optical materials, membrane materials for separation, Langmuir–Blodgett (LB) films, opto-electronics, liquid crystal alignment, composites, electroluminescent devices, EC materials, polymer electrolyte fuel cells, polymer memories, fibre optics, etc. Their widespread application is the result of not only their unique physical properties but also the ease of their synthesis. The polymerisation is usually done in a two-step method. The first step involves a very fast, exothermic, stepwise polymerisation at a relatively low temperature to form a poly(amic acid) from a dianhydride and a diamine. Subsequently, the poly(amic acid) is converted into the corresponding PI through an intramolecular cyclisation (imidisation) that releases water condensate [12].

The synthesis, properties and applications of PIs have been reviewed from different perspectives. For example, Liaw et al. [12] reviewed organosoluble PIs; Sroog [13] reviewed aromatic and heterocyclic PIs; Mehdipour-Ataei and Bahri-Laleh reviewed pyridine units containing PIs [14], and PI electrochemical properties have been reviewed by Viehbeck and Kovac [15].

To the best of our knowledge, Mazur et al. [16] were the first scientists to research the electrochromism of aromatic PIs. These scientists found that aromatic PIs are potential electrochromes, as the optical absorption of the aromatic PIs changed with the potential applied. PIs demonstrate high electrical resistivity, a low dielectric constant, and low permeability towards ions, but they can also transport both ions and electrons at significant rates. Two factors are responsible for these conflicting characteristics. First, the aromatic diimide group can function as an electron acceptor, undergoing two independent one-electron redox reactions, much like a quinone. Second, the polymer is prepared by what amounts to solid-state chemistry and has a very high glass transition temperature (T_g). Consequently, such physical properties as solvent swelling and ion permeability are sensitive to the thermal and chemical history of the sample and can be varied rather dramatically.

2.1. Triphenylamine

A popular way to obtain charge-transporting polymers is by incorporating TPA and its derivative units into the main chain, which provides electroactive sites because they are electron-rich aromatics and readily oxidised to form radical cation-conducting salts [17]. To the best of our knowledge, the first PI containing TPA was prepared by Vasilenko et al. [18] in 1991, followed by Nishikata et al. [19], who prepared PIs containing TPA derivatives with a methoxy substituent in the para position. The methoxy substituent in the para position is important because TPA derivatives could be dimerised during the anodic oxidation pathway [20], which can be prevented by incorporating electron donating groups at the para position, which also creates stable cationic radicals with lower potential [21].

In 2002, the incorporation of a TPA derivative into PIs was reported by Liaw et al. [17]. Liaw et al. wrote the first paper describing the EC property of PIs containing TPA derivatives. The PIs have methyl groups at the para and meta positions (see Fig. 1 5a–f). The polymer T_{d10} values are from 430 to 566 °C and 462–574 °C in N_2 and air atmospheres, respectively. Most of the polymers showed higher T_{d10} values in air than in a nitrogen atmosphere, possibly because of the oxidation of methyl groups in the polymer chain, which causes weight gain. These polymers afforded a high anaerobic char yield in the range of 63–72% at 800 °C under a nitrogen atmosphere. They transformed from yellow (neutral) to blue (oxidised). The properties of the prepared PIs can be seen in Table 1.

Liaw's group has also synthesised another series of PIs containing the parent TPA and its derivatives, bis-2-phenyl-2-isopropylbiphenyl [22] (see Fig. 1, polymer 5a–f). The polymer changed colour from pale yellow to green to blue (see 2 in Table 2), Current consumption, potential step absorption and EC behaviour were illustrated in Fig. 3. Many papers in the literature [23,24] proposed that the first oxidation was related to the electron removal of the lone pair from nitrogen. However, electron removal of the lone pair from nitrogen is not sufficient to explain the oxidation of triarylamine-containing polymers. By using computational studies, it was shown that the electron density distribution of HOMO state of basic unit (ground state) was located to the conjugation, and the electronic density contours show that the electron lone pair of the nitrogen atoms have strong coupling with the π electrons of the benzene ring. They can not be considered separately. Therefore, a more reasonable explanation is that the first oxidation was found to remove the electron from the HOMO of

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