

# A facile approach to multicolored electrochromic triarylamine-based thermoset epoxy materials with tunable intervalence charge transfer behavior†

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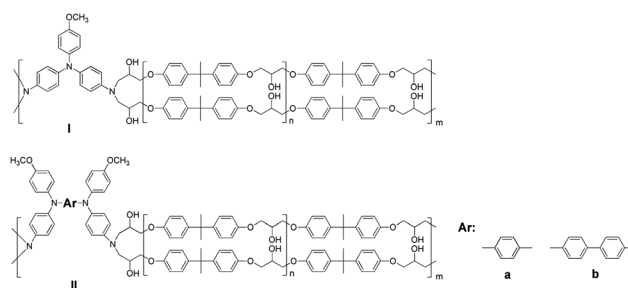
**By a facile curing reaction, novel electrochromic triarylamine-based thermosetting epoxy materials could be readily prepared for the first time. The resulting multielectrochromic epoxy materials exhibited good electrochemical stability and large optical changes in transmittance between their bleached and colored states with tunable intervalence charge transfer behavior.**

Electrochromic (EC) materials exhibit a reversible optical change in absorption or transmittance upon electrochemical oxidation or reduction; the EC effect has been known for quite some time, and great strides have been made with transition metal oxides (*e.g.*, WO<sub>3</sub>), inorganic coordinating complexes, organic molecules, and electrodeposited  $\pi$ -conjugated polymers films.<sup>1</sup> The earliest EC devices were mostly based on inorganic oxides, nevertheless, organic materials have several advantages over these, such as processability, high coloration efficiency, fast switching ability, and multiple coloring within the same material. Initially, investigation of EC materials was directed towards optical changes in the visible light region (*e.g.*, 400–800 nm) and demonstrated useful and variable applications such as E-paper, optical switching devices, smart windows, and camouflage materials.<sup>2</sup> Increasingly, attention to optical changes has been focused extensively from the near infrared (NIR; *e.g.*, 800–2000 nm) to the microwave regions of the spectrum, which can be exploited for optical communication, data storage, and thermal control (heat gain or loss) in buildings and spacecraft.<sup>3</sup> Since 2002, our group has reported several triphenylamine (TPA)-containing EC polymers with interesting multicolor transitions<sup>4</sup> that showed good EC reversibility in the visible region and NIR range.

According to Lee and Neville,<sup>5</sup> thermosetting epoxy resins exhibit high toughness, low shrinkage, excellent adhesion, and good corrosion resistance, and are widely used in coatings,

adhesives and composite materials. In addition to these advantages, epoxy resins are also commercially available materials with a competitive price, thus they are good candidates as EC materials for practical applications. However, the TPA-based electrochromic thermoset epoxy materials derived from diamines with triarylamine structures as the curing agent have not been prepared and investigated until now. Furthermore, these TPA-containing diamines could not only be the hardeners of the epoxy resins without adding any other accelerators, but also effectively increase the oxidation sites of the resulting thermoset EC epoxy materials when compared with their corresponding polyamides. TPA groups could be expected to impart flame retardant properties to the epoxy resin due to the high aromatic content. Moreover, considering the environmental issue, these systems could be seen as “green” since they are halogen free and phosphorus free.<sup>6</sup> In this study, we try to introduce three TPA-based diamines, 4,4'-diamino-4''-methoxytriphenylamine (**1**),<sup>4a</sup> *N,N'*-bis(4-aminophenyl)-*N,N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (**2a**)<sup>4c</sup> and *N,N'*-bis(4-aminophenyl)-*N,N'*-di(4-methoxyphenyl)-4,4'-biphenyldiamine (**2b**),<sup>4f</sup> as the hardeners into a diglycidyl ether of bisphenol A (DGEBA) (from Nan Ya Plastics Corporation), which is a commercial epoxy resin formulation with equivalent weight of epoxidic component (epoxy equivalent weight, EEW) of 185.0–186.6 g per eq., to obtain novel EC thermoset epoxy materials (Scheme 1). We anticipated that the prepared EC thermoset epoxies should have excellent thermal properties, good electrochemical

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**Scheme 1** Chemical structures of the electrochromic thermoset epoxies.

stability, and high optical transmittance contrast ( $\Delta T$ ) in both the visible and NIR region.

Thermoset epoxies were prepared by reacting DGEBA with various diamines of TPA derivatives at an equivalent ratio of 2:1 in *N,N*-dimethylacetamide (DMAc) *via* a thermal curing method (Scheme S1, ESI†). The detailed synthetic procedure is described in the ESI.† After the curing processes, the exothermic peak disappeared in DSC measurement implying the completed curing reaction (Fig. S1, ESI†).

The thermal properties of electrochromic thermoset epoxies were examined by TMA, TGA, DMA, and the results are summarized in Table 1. All the prepared epoxy materials exhibited good thermal stability with insignificant weight loss up to 360 °C under a nitrogen atmosphere (Fig. S2, ESI†). The carbonized residues (char yield) of the thermoset epoxy materials were more than 18% at 850 °C. The high char yields of these thermoset epoxies could be ascribed to their high aromatic content. The softening temperature ( $T_s$ ) 111 °C, 141 °C, and 143 °C of the resulting epoxy materials **I**, **IIa** and **IIb** could be easily measured by the TMA thermograms (Fig. S3, ESI†). The glass transition temperature  $T_g$  around 155–173 °C could also be obtained by DMA measurement (Fig. S4, ESI†).

The electrochemical properties of the cured TPA containing epoxy materials were investigated by cyclic voltammetry (CV) conducted by the cast film on an indium-tin oxide (ITO) coated glass slide as the working electrode in anhydrous acetonitrile ( $\text{CH}_3\text{CN}$ ), using 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte under a nitrogen atmosphere. Before electrochemical measurement, prescanning was utilized to ensure the thermoset epoxy thin films were in a saturated state. Fig. 1 depicts the typical CV diagrams of **I**, **IIa** and **IIb** for comparison; there are two reversible oxidation redox couples for all the prepared epoxy materials. Furthermore, less reversible third and fourth oxidation steps for **I** and **II** could be observed between 1.0 to 2.0 V, respectively. After 100 continuous cyclic scans, all the thin films still exhibited good electrochemical stability at the first oxidation stage. All the data on electrochemical properties are summarized in Table 2. During the electrochemical oxidation of epoxy thin film **I**, the color changed from colorless to green, blue-green and then deep blue. In addition, the color of thin film **IIa** changed from colorless to light green, light blue, dark blue, and then blue black. The coloring phenomenon of thin film **IIb** was very similar to the thin film **IIa**. Compared with their corresponding polyamides,<sup>4a,c,f</sup> introduction of TPAs into DGEBA

**Table 1** Thermal properties of thermoset epoxies

| Code       | $T_s^a$ (°C) | $T_g^b$ (°C) | $T_d^{5c}$ (°C) |     | $T_d^{10c}$ (°C) |     | Char yield <sup>d</sup> (wt%) | LOI <sup>e</sup> |
|------------|--------------|--------------|-----------------|-----|------------------|-----|-------------------------------|------------------|
|            |              |              | N <sub>2</sub>  | Air | N <sub>2</sub>   | Air |                               |                  |
| <b>I</b>   | 111          | 155          | 360             | 335 | 385              | 380 | 18                            | 25               |
| <b>IIa</b> | 141          | 170          | 385             | 380 | 405              | 410 | 23                            | 27               |
| <b>IIb</b> | 143          | 173          | 360             | 350 | 375              | 380 | 24                            | 27               |

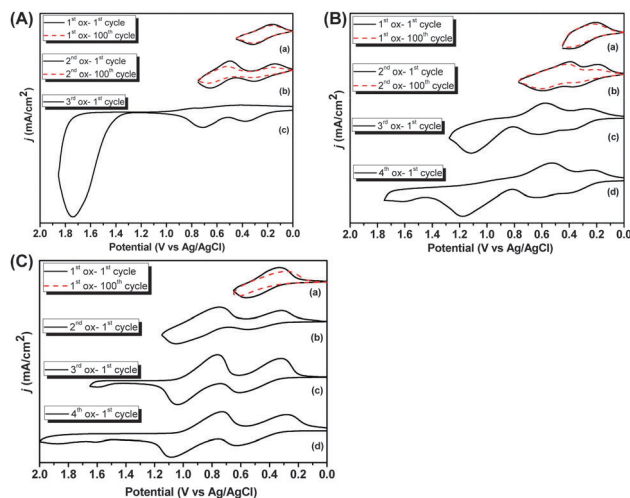
<sup>a</sup> Softening temperature measured by TMA in penetration mode.

<sup>b</sup> Glass transition temperature was performed by DMA on the obtained specimens (30.0 mm long, 1.00 mm wide, and 0.30–0.56 mm thick).

<sup>c</sup> Temperature at which 5% and 10% weight loss occurred, respectively, recorded by TGA.

<sup>d</sup> Residual weight percentage at 850 °C in nitrogen.

<sup>e</sup> LOI = Limiting Oxygen Index =  $(17.5 + 0.4 \times \text{char yield})$  at 850 °C.



**Fig. 1** Cyclic voltammograms of epoxy material (A) **I** ( $215 \pm 15$  nm in thickness) (B) **IIa** ( $180 \pm 10$  nm in thickness) and (C) **IIb** ( $240 \pm 20$  nm in thickness) films for each oxidation stages on an ITO-coated glass substrate over cyclic scans in 0.1 M TBAP/ $\text{CH}_3\text{CN}$  at a scan rate of  $50 \text{ mV s}^{-1}$ .

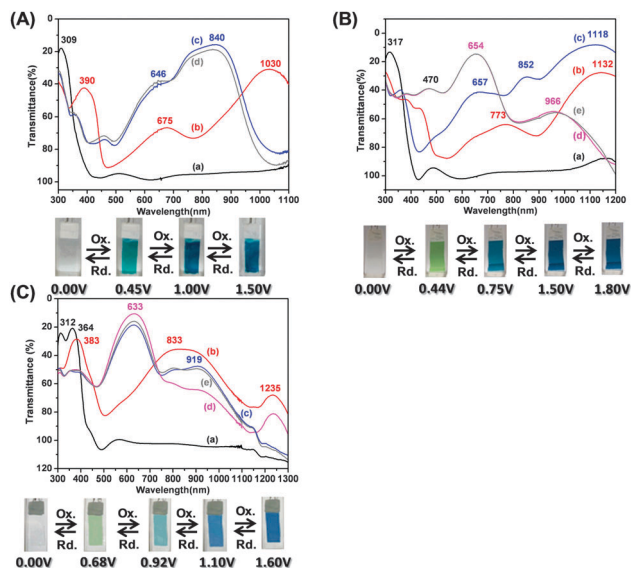
**Table 2** Electrochemical properties of thermoset epoxies

| Code       | Oxidation potential <sup>a</sup> (V) |                       |                       |   |   |
|------------|--------------------------------------|-----------------------|-----------------------|---|---|
|            | $E_{\text{onset}}$                   | $E_{1/2(\text{ox}1)}$ | $E_{1/2(\text{ox}2)}$ | $E_{\text{p}(\text{ox}3)}$ <sup>b</sup> | $E_{\text{p}(\text{ox}4)}$ <sup>b</sup> |
| <b>I</b>   | 0.16                                 | 0.24                  | 0.58                  | 1.74                                    | —                                       |
| <b>IIa</b> | 0.16                                 | 0.28                  | 0.49                  | 1.17                                    | 1.61                                    |
| <b>IIb</b> | 0.32                                 | 0.44                  | 0.92                  | 1.10                                    | 1.61                                    |

<sup>a</sup> From cyclic voltammograms *versus* Ag/AgCl in  $\text{CH}_3\text{CN}$ . <sup>b</sup> Peak potential of the irreversible oxidation step.

could effectively increase the number of oxidative stages of the cured epoxy materials and reveal multi-electrochromic behaviors.

Spectroelectrochemical experiments were used to evaluate the optical properties of the EC films. For the investigations, the thermoset epoxy films were cast on an ITO-coated glass slide, and a homemade electrochemical cell was built from a commercial ultraviolet (UV)-visible cuvette. The cell was placed in the optical path of the sample light beam in a UV-vis spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in a 0.1 M TBAP- $\text{CH}_3\text{CN}$  solution. The results of TPAs/DGEBA films were presented in Fig. 2 as a series of UV-vis absorbance curves correlated to electrode potentials. In the neutral form (0 V), these colorless epoxy films **I**, **IIa** and **IIb** exhibited a strong TPA characteristic absorption at 309, 317, and 312 nm, respectively. Upon oxidation of epoxy material **I** shown in Fig. 2(A) (increasing applied voltage from 0 to 0.45 V), the intensity of the absorption peak at 309 nm gradually decreased, whereas new peaks at 390 nm and 675 nm, and a broad band with its maximum absorption wavelength at 1030 nm in the NIR region gradually increased in intensity. We attribute the spectral change in visible-light region to the formation of monocation radical of TPA moiety. In addition, the broad absorption in the NIR region was the characteristic result due to IV-CT excitation associated with electron transfer through the phenyl bridge between the active neutral nitrogen atom to the cation radical



**Fig. 2** Electrochromic behavior of aromatic thermoset epoxy materials (A) thin film **I** ( $215 \pm 15$  nm in thickness) on the ITO-coated glass substrate in 0.1 M TBAP/ $\text{CH}_3\text{CN}$  at applied potentials of (a) 0.00, (b) 0.45, (c) 1.00, (d) 1.50 (V vs. Ag/AgCl), (B) thin film **IIa** ( $180 \pm 10$  nm in thickness) on ITO-coated glass substrate in 0.1 M TBAP/ $\text{CH}_3\text{CN}$  at applied potentials of (a) 0.00, (b) 0.44, (c) 0.75, (d) 1.50, (e) 1.80 (V vs. Ag/AgCl), and (C) thin film **IIb** ( $240 \pm 20$  nm in thickness) on the ITO-coated glass substrate in 0.1 M TBAP/ $\text{CH}_3\text{CN}$  at applied potentials of (a) 0.00, (b) 0.68, (c) 0.92, (d) 1.10, (e) 1.60 (V vs. Ag/AgCl).

central nitrogen of the TPA moiety, implying electron delocalization in these cation radicals, which is consistent with the phenomenon classified by Robin and Day.<sup>7</sup> When the potential was adjusted to more positive values 1.00 V and 1.50 V corresponding to the second and third oxidation, a characteristic new peak at around 840 nm appeared. The obvious decrease of the absorbance in the NIR region might be attributed to the formation of a *p*-phenylenediamine quinonoid-type dication after a second oxidation occurred at the dialkyl substituted amino groups of the *para*-phenyl positions within TPA moiety thus eliminated the IV-CT. Compared with epoxy material **IIa** in Fig. 2(B) by increasing the applied potential from 0 to 0.44 V, the intensity of the absorption peak at 317 nm gradually decreased, while new peaks at 773 and 1132 nm gradually increased in intensity. The broad absorption wavelength around 1132 nm in the NIR region resulted from the IV-CT excitation of epoxy material **IIa** is similar to the behavior of epoxy material **I** film. As the anodic potential keep increasing to 0.75 V, the nitrogen atom of dialkyl substituted amino groups was oxidized resulting in stronger IV-CT behaviour. If the applied potential was increased further to 1.5 V, the absorption bands of the cation radical decreased gradually with a new broad band centered at around 655 nm. The disappearance of the NIR absorption band could be attributed to the further oxidation from monocation radical species to the formation of quinonoid-type dication at the other nitrogen atoms of the

dialkyl substituted amino groups. When the oxidation potential applied was more positive at 1.8 V, the NIR region absorbance decreased almost completely just as the case of the third oxidation stage of epoxy material **I** film. In addition, epoxy material **IIb** showed a similar spectroelectrochemical tendency to epoxy material **IIa** (shown in Fig. 2(C)). The apparent difference is that epoxy material **IIb**, cured by the diamine with a tetraphenyl-substituted benzidine unit, has a longer distance between the two electroactive nitrogen sites than in the case of the substituted *p*-phenylenediamine. This reveals weaker electronic interaction absorption of IV-CT at a wavelength of 1235 nm in the NIR region than **IIa**. The results demonstrate a facile approach for tuning the IV-CT behavior in the NIR range.

In summary, novel multi-electrochromic TPA-containing thermosetting epoxies have been readily prepared by using triarylamine-containing diamines as a curing agent. To the best of our knowledge, this is the first time that it has been demonstrated that EC thermoset epoxy materials can be obtained *via* such a facile approach. These different EC TPA-based epoxy materials exhibited good electrochemical stability, interesting multi-electrochromic behavior, highly optical contrast both in the visible and NIR region between their bleached and colored states. Furthermore, the absorption in the NIR also could be tuned by adjusting the IV-CT capability of the diamine curing agent with different triarylamine-containing structures. This study opens up a new potential application of functional thermoset epoxy materials.

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