Polymeric electrochromics

Gursel Sonmez

Conducting polymers are excellent candidates for applications in displays, mirrors, windows, light-emitting diodes, photovoltaics, near-infrared devices and electrochromic devices. From these potential applications, in this article, we will focus on the electrochromic polymers and devices. Although several objective studies have been conducted in the last decade, bringing to light many advantages over other types of electrochromics, polymeric electrochromics have not yet received the industrial attention that they deserve. One of the most important and dazzling advantages of polymers over the other types of electrochromics is the ease of modification of a polymer's backbone, that changes almost the entire properties of the material and switches many disadvantages into advantages. Our recent completion of the deficient third leg of additive primary colour space was a very good example of tailoring the polymer backbone. This discovery could be considered as one of the milestones of commercialization of polymeric electrochromics. In this article, we will also discuss the completion of the additive primary colours, red, green and blue (RGB), in polymeric electrochromics and their ways of commercialization.

Introduction

Following the discovery of the first electrically conducting polymer, poly(acetylene),[1] electroactive conjugated polymers

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have received great attention in many fields of application. The follow-up discoveries have resulted in their commercialization, with applications in electrochromic mirrors,[2–4] windows,[5–7] thin-film transistors,[8] displays,[9,10] sensors,[11,12] polymer light-emitting diodes,[13] photovoltaics,[14] near-infrared devices[15–17] and electrochromic devices.[18–24] Recently, the research on conjugated polymers has mostly been focused on the optical properties of these materials in visible and near-infrared (NIR) regions.[15–17,19,25]

Initial studies of electrochromic devices began with inorganic compounds such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2).[26,27] Then, organic materials, such as viologens, metallophthalocyanines and conducting polymers, received much attention for electrochromic applications.[28] The different colours observed with these compounds while switching between their different redox states is one of the most important advantages of organic materials.[29] Among the organic electrochromic materials, conducting polymers have received more attention because of their additional advantages over inorganic compounds, such as outstanding coloration efficiency,[22] fast switching ability,[30,31] multiple colours with the same material[19,22,32,33] and fine-tuning of the band gap (and the colour) through chemical structure modification.[18,24,34,35–37]

The contradiction between the effort of research in electrochromic conjugated polymers and their industrial application is surprising. Although polymeric electrochromics have been studied very actively in the last decade, they have not yet received the industrial attention that they deserve. For commercial applications of these materials, stability, rapid response times, optical density changes, percent transmittance or luminance changes, low power requirements, highly efficient colour changes and ease of structural modification for colour tuning are some of the important parameters.[22,38] Recent improvements in some of these application requirements should be taken into consideration for commercialization.

Substitution within a conjugated polymer's backbone with electron donating alkoxy substituents, for example, had a remarkable influence on electrical, electrochemical and optical properties.[20,22,39–43] Coloration efficiency, defined as the relationship between the injected/ejected charge as a function of electrode area and the change in optical density units,[22,44,45] is one of these properties. Electrochromic materials could be employed for the fabrication of very rapid, efficient displays and light modulators if they could exhibit sufficiently high coloration efficiency. The ideal device should exhibit a large change in transmittance with a small increase in charge, giving rise to large coloration efficiency values. In comparing coloration efficiency values of the electrochromic materials to date, conducting polymers are far ahead of the inorganic solids.[22] The reported values of coloration efficiency for inorganic materials and conducting polymers were in the ranges of 10–50 and 30–700 cm^2 C^{-1}, respectively.[22] This shows that use of conducting polymers as electrochromics results in an increase by one order of magnitude of coloration efficiency over inorganic molecules. The wide range of coloration efficiency values in conducting polymers is a very good example for the enhancement of polymer properties by backbone modification. In the course of our investigations, we have shown that addition of a methoxy ethylhexyloxy benzene group between two 3,4-ethylenedioxythiophene units on the polymer backbone improved the facility of counterion injection/rejection, generating higher doping levels and coloration efficiency values than poly(3,4-ethylenedioxythiophene).[22]

In electrochromic materials, electrochemical oxidation or reduction induces a reversible change in the reflected or transmitted light, which is defined as electrochromism. The stability of the electrochromic materials while switching between their different oxidation states is another crucially important feature for practical use of these materials for any purposes. Electrochromic materials should switch between their oxidized and reduced states (or different oxidation states that produce different colours) with a certain lifetime. Compared to the other types of electrochromic materials, polymers are very promising in terms of their stability upon multiple switching.[18,24,46] For example, it was shown that a sealed polymeric electrochromic device under an inert atmosphere could be switched 180 000 times with an only 6% loss of its total 75% optical contrast.[46]

Realization of RGB colours in polymeric electrochromics

In the history of polymeric electrochromics, the discovery of the deficient third leg (green) of additive primary colour space was probably one of the most important steps for the commercialization of these materials. Having the three additive primary colours, red, green and blue (RGB), in polymeric electrochromics makes many things easier. Although many red and blue coloured polymers in their neutral states have been reported before, until recently no green coloured conducting polymer had been reported because of the difficulty in obtaining the absorptions required in the visible region to reflect the green colour. In 2004 we reported electrochemical and optical properties of the first neutral,

green coloured conjugated polymer.[18] The extreme stability of this polymer after 10 000 double potential steps makes it the best candidate, so far, for completing the third leg of RGB colour space in polymeric electrochromics. It is important to note that modification of a conjugated polymer's backbone can produce many differently coloured polymers, as successfully demonstrated by Reynolds' group.[30,32] Using different polymers in their neutral, intermediate and doped states produced a variety of colours.[32] On the other hand, according to colour mixing theory, it would also be possible to obtain all colours required for commercial electrochromic applications of conjugated polymers, once additive or subtractive primary colours are available.[19] Theoretically, if two colour stimuli are mixed, the resulting colour stimulus will lie somewhere along the straight line connecting the two points on the chromaticity diagram. The position of the point depends on the ratio of the amounts of the two mixed colours. A "fine-tuning" of colour is possible by adjusting film thickness, which has a large influence on the colour due to its effect on the brightness of the transmitted light. For use in displays, polymers should switch between one of the three primary colours and their transmissive states. Unfortunately, as stated above and in our previous study,[18] most of the polymers studied so far mainly absorb/reflect blue and red colours in their neutral states. Since absorption at only one dominant wavelength is enough to get blue or red colours, it is relatively easy to get these colours by tuning the band gap of conducting polymers. For a green coloured conducting polymer, at least two chromophores are required that absorb at two different wavelengths, where blue and red colours absorb. While these chromophores absorb red and blue colours in the neutral form of polymer, they should also deplete together when the polymer is oxidized. Unfortunately, controlling both chromophores at the same time with the same applied potential is very difficult. This difficulty in controlling two absorption bands in the visible region from the same polymer, delayed the realization of the first neutral green polymer.

We have designed a monomer, 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine (DDTP), that has two chromophores. Successful electrochemical and chemical polymerizations of DDTP via its terthiophene unit produced a material [PDDTP] that reflected green light in the neutral state and was transmissive in the oxidized state.[18] Dioctyl substitution of DDTP produced a soluble green electrochromic conjugated polymer, poly{5,7-bis(3-octyl-thiophen-2-yl)-2,3-dithiophen-3-yl-thieno[3,4-b]pyrazine}, in its neutral form as well.[47] A combination of the green polymeric electrochromic with other red [*i.e.*, poly(3-alkyl-thiophene)s, poly(3,4-ethylenedioxypyrrole), poly{2-methoxy-5-(2′-ethylhexyloxy)paraphenylene vinylene},...] and blue [*i.e.*, poly(3,4-ethylenedioxythiophene), poly(benzo[c]thiophene), poly(3,3-dialkyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine),...] polymers completes the additive primary colour space. Fig. 1 depicts the structures and absorption spectra of polymers that complete the three additive primary colours. Poly(3-methylthiophene) or poly(3-hexylthiophene) (**1**), PDDTP (**2**) and poly(3,4-ethylenedioxythiophene) (PEDOT) (**3**) were used as red, green and blue colours, respectively. RGB polymers for spectroelectrochemistry were prepared
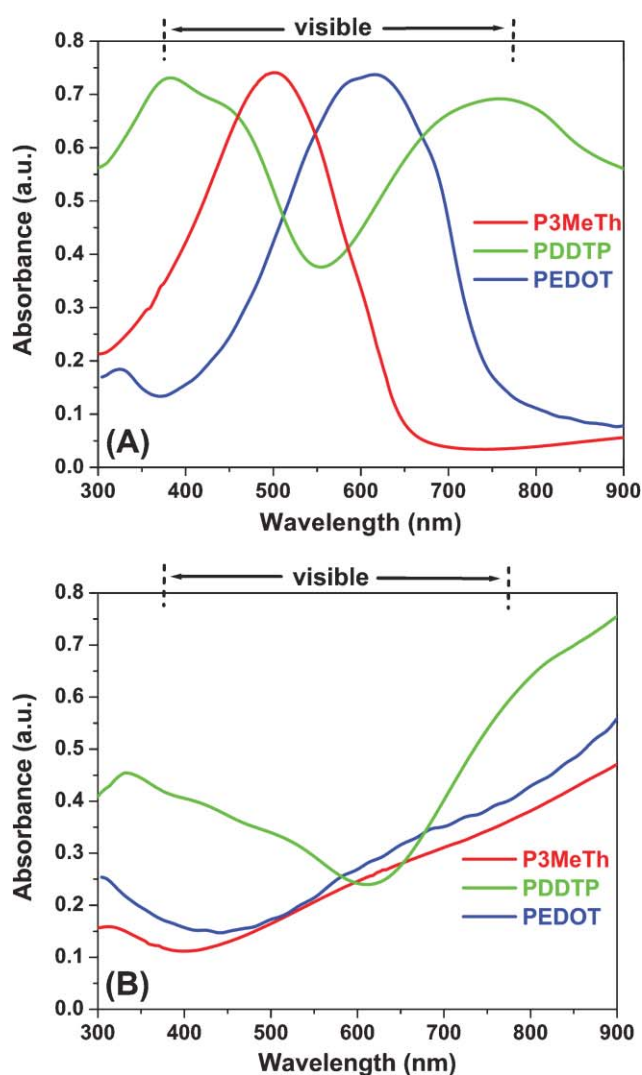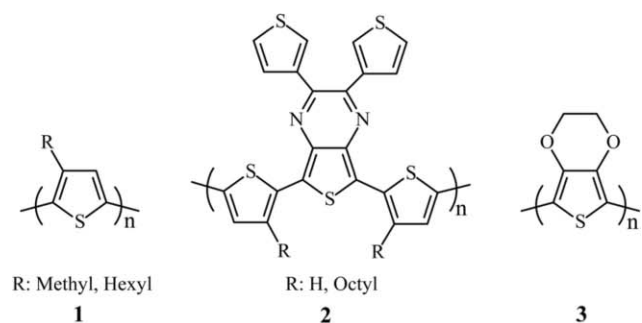
Fig. 1 (Top) Structures of the polymers used for completing the additive primary colours, RGB: **1**: poly(3-methylthiophene) or poly(3-hexylthiophene); **2**: poly{2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno-[3,4-*b*]pyrazine} and poly{5,7-bis-(3-octyl-thiophen-2-yl)-2,3-dithiophen-3-yl-thieno[3,4-*b*]pyrazine}; **3**: poly(3,4-ethylenedioxythiophene). (Bottom) Combined spectroelectrochemistry of **1**, **2** and **3** in the (A) neutral and (B) oxidized forms of the polymers.

electrochemically on indium tin oxide (ITO)-coated glass slides according to the procedure explained previously.[18] Here, polymers **1** and **3** have absorption maxima in the visible region at 500 and 615 nm, reflecting red and blue colours,

respectively. These films switch at these wavelengths between their coloured and bleached states. On the other hand, **2** absorbs in the regions below and above 550 nm with a valley (absorption minimum) at this wavelength and maxima at 380 and 760 nm, reflecting a very saturated green colour (Fig. 1A). These two absorptions act together during both coloration and depletion of polymer's colour. A combination of these three spectra covers the entire visible region without reflecting any light that produces a black colour. Having absorption maxima at different wavelengths in the visible region is one of the big advantages of these three polymers. There are differences in wavelength of *ca.* 120 nm between the absorption maxima of the three polymers in the visible region, that prevent the interference of the main absorptions.

As RGB coloured polymers are oxidized their colours deplete, producing pale blue colours for the polymers **1** and **3** and a transmissive brown colour for polymer **2** (Fig. 1B). It should frankly be noted that, although the polymers, **1**, **2** and **3**, have highly saturated RGB colours in their neutral forms, the residual pale brown colour of **2** in the oxidized form is still a problem in applications and needs to be improved. The red and blue coloured polymers have almost the same spectrum in their oxidized states. If the green polymer can also produce a similar spectrum to the red and the blue coloured polymers in its oxidized state, then using a proper colour filter brings all the RGB colours to the white point (W) in the CIE (Commission Internationale de l'Eclairge = International Commission on Illumination) colour space. The optical contrasts (%ΔT) for red (**1**) and blue (**3**) coloured polymers are *ca.* 53% and 55% at their dominant wavelengths in the visible region. The green polymeric electrochromic (**2**) shows relatively low optical contrasts at its absorption maxima in the visible region compared to those of the red and the blue coloured polymers. It has 23% and 12% of transmittance change (%ΔT) at wavelengths 370 and 725 nm, respectively. Enhancement of this low optical contrast will obviously improve the material's properties and will make it more transparent in its oxidized state. As an additional advantage for these three polymers, they all have more than 80% optical contrast in the NIR region, making them useful for applications in NIR devices as well.[15–17]

The realization of the RGB colours in polymeric electrochromics completed the three legs of the CIE 1931 colour space as shown in Fig. 2A. The polymers, **1**, **2** and **3**, in their neutral states reflect saturated red, green and blue colours, respectively. Upon oxidation, they switch towards their transmissive colour states, in other words, towards the white point (W) in CIE 1931 colour space. The time required to switch the polymers **1**, **2** and **3** together from their highly saturated RGB colours to their transmissive colours is less than 2 seconds. It is important to note that this switching time is too long for applications and should not be considered as the response time of each individual polymer. Interestingly, these polymers have similar potential windows for oxidation and reduction processes. Thus, they all complete their full switches in a potential window of less than 1.5 V. But, in this potential window, each polymer has a certain narrow window in which it completes more than 90% of its switching as discussed below (Fig. 4). The given time of switching (<2 seconds) is the total
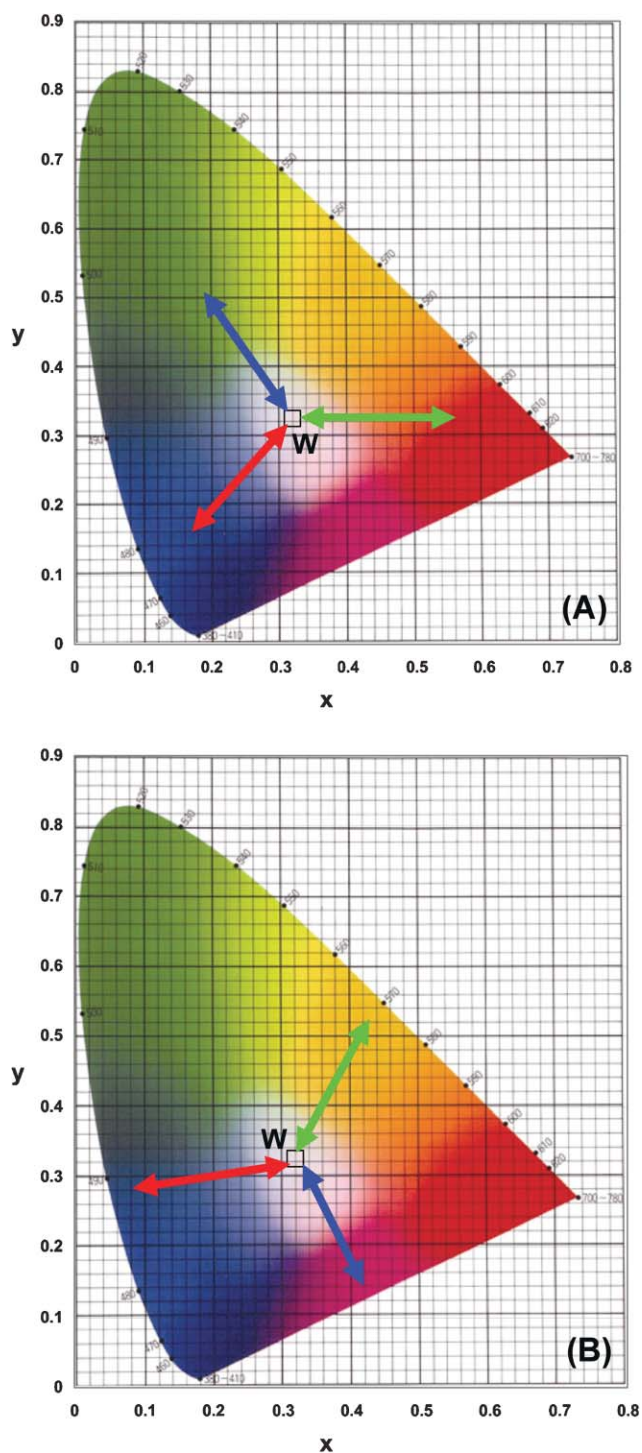
Fig. 2 CIE 1931 colour space. (A) Polymers switch from additive primary colours, red, green and blue (RGB) to the white point (W). (B) Polymers switching from subtractive colours, cyan, magenta and yellow (CMY) to the white point.

time in which all polymers complete their switches from the same voltage source.

Completion of the subtractive colour space as shown in Fig. 2B should certainly be the next step for research in polymeric electrochromics. For this, three polymers are required that have saturated cyan, magenta and yellow

(CMY) colours. They should also act together to switching from these CMY colours to their transmissive states, close to the white point in CIE 1931 colour space. So far, to the best of our knowledge, polymers reflecting yellow and magenta are available and a cyan colour waits for discovery. We believe, in addition to the polymers reflecting additive primary colours, having subtractive primary colours in polymeric electrochromics will accelerate the use of these materials in many applications.

Spectroelectrochemistry and colour

When the spectroelectrochemistry of polymeric electrochromics is investigated, it is seen that all polymers produce different spectra in the ultraviolet (UV), visible and NIR regions. High and low band gap polymers have π–π* transitions in the UV and NIR regions, respectively. Since our eyes are not sensitive to these regions, not all optical changes in π–π* transitions can be followed with the naked eye. As a result, these polymers are not very useful for polymeric electrochromic devices. Only, some of the high band gap polymers having their π–π* transitions in the UV region find applications because of their absorption changes in the visible that correspond to low energy charge carriers (polarons and bipolarons).[24,34] The majority of conjugated polymers with band gaps between 1.0 and 2.5 eV usually present their π–π* transitions in the visible region. Attentive studies of the spectroelectrochemistry of conducting polymers showed that they have an extra advantage over other types of electrochromics. Although most of the other electrochromic materials only switch between two oxidation states (neutral and oxidized), conducting polymers can be controlled between these two extreme oxidation states with applied potentials. This means a single polymeric electrochromic film can produce different absorptions at different oxidation states, resulting in different tones of the same colour, or sometimes different colours, with small variations in the applied electrical voltages. Fig. 3 clearly demonstrates this behaviour for a well-known polymer, PEDOT. Neutral PEDOT films absorb in the visible region, displaying a maximum at 615 nm associated with π–π* transitions, producing a deep blue colour. Upon oxidation, π–π* transition depletes at the expense of a broad peak outside the visible region at longer wavelength, corresponding to low energy charge carriers (radical cations and dications). When the polymer film is completely oxidized, it turns to a pale blue (sky blue) colour.

A stepwise switching of the PEDOT film with small increments of the applied potential changes its oxidation state, resulting in different intensities of absorption at the same wavelength (Fig. 3, left). As a result of this, the polymer produces different tones of blue colour as shown in Fig. 3, right. This stepwise oxidation of PEDOT film between its fully neutral (−0.9 V, dark blue colour) and fully oxidized (+1.0 V, sky blue colour) states produces at least 20 oxidation steps. These steps can easily be controlled by the applied potentials and followed with a spectrophotometer, resulting in different intensities of the same polymer's absorption at the same wavelength in the visible region. Since each of these absorptions corresponds to colour, a single polymer film can produce
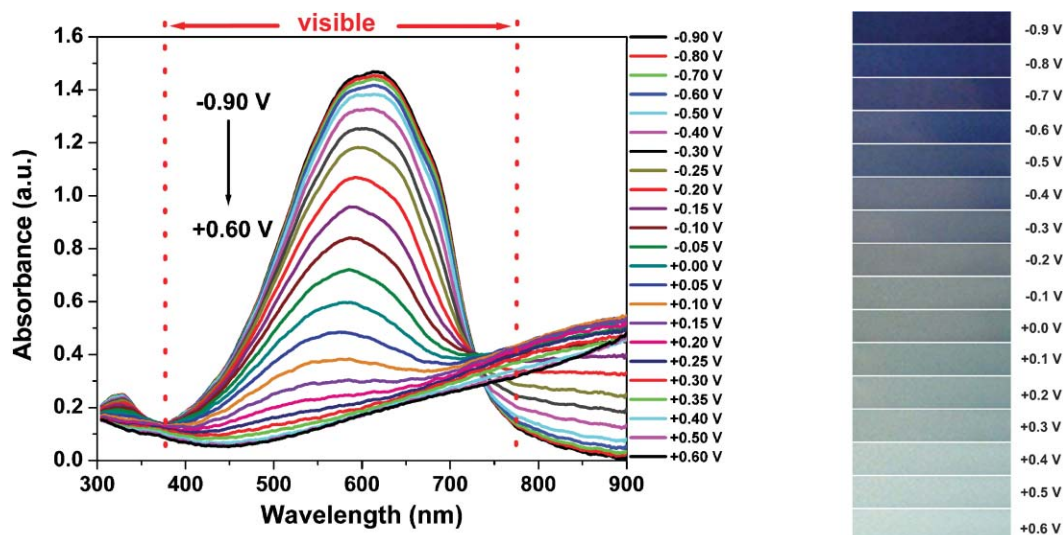
Fig. 3 (Left) Spectroelectrochemistry of PEDOT film: optical variation in the visible region as a function of applied potentials. (Right) Applied potential dependence of the blue colour produced by PEDOT films.

more than 20 different shades of the same colour. It should be noted that our eyes are not sensitive enough to recognize all of these optical changes. Especially, optical changes at the applied potentials above +0.30 V and below −0.60 V are very small and very difficult to distinguish with the naked eye. For this reason, in Fig. 3, right, we only present the polymer colours produced with 0.1 V applied potential increments between −0.9 and +0.6 V. Depletion of PEDOT's dark blue colour upon oxidation can easily be followed from these pictures. The polymer film changes its colour from a dark blue to the sky blue with intermediate colours (other tones of blue) between these two extreme points.

Revision of the optical properties of a polymer film in comparison with its cyclic voltammogram (CV) gives information about the polymer's behaviour. Fig. 4 depicts the CV of the PEDOT film that produces the optical spectra given in Fig. 3. When the potential variations in the CV (Fig. 4) and corresponding optical changes (Fig. 3) in the polymer film are compared, the potential variations in the CV of the polymer film can be divided into six regions. In the first region (I), as the potential was swept from −1.7 V to −0.9 V, there was almost no change in the currents as well as the absorption spectrum. In this region of the applied potentials, the polymer film was in its neutral non-conducting form, generating a strong absorption in the visible region associated with π–π* transitions. In the second region (II), where the potential was swept from −0.9 V to −0.7 V, the polymer film started to oxidize, generating currents in the CV, and small optical changes in the visible region were observed. The applied potentials in this region can be considered as the onset potentials of oxidation.[34] Although an increase of 0.06 mA cm^{-2} was seen in the current density in this region, the total optical change (%ΔT) was only 0.24%. The third region (III) is the potential window where a current ramp starts because of the polymer's oxidation. In this region, although a reasonable increase in the current density was seen (0.32 mA cm^{-2}), the optical changes resulting from this much charge injection were just 0.47%. Sweeping to more positive potentials after this

point (−0.5 V) started to cause dramatic changes in the optical properties of the polymer film. This potential window (region IV) is also the region where the half wave potential ($E_{1/2}$) of the polymer is located. Almost all optical changes in the polymer film occurred in this region (between −0.5 V and +0.25 V). The total optical contrast in the polymer film resulting from the potential sweep between −0.50 V and +0.25 V was about 55%. Between the potentials of +0.25 V and +0.50 V (region V), the polymer film was about to complete its oxidation, resulting in the final residual optical changes in the film. In this region, the polymer film showed *ca.* 4% of transmittance change. Above the potentials of +0.50 V *vs.* Ag/Ag$^+$ (region VI) the oxidation process was completed. A plateau of the curve was seen, resulting from capacitive currents which no longer affected the optical properties of the polymer film unless overoxidation. If the polymer film is exposed to high potentials (overoxidation),
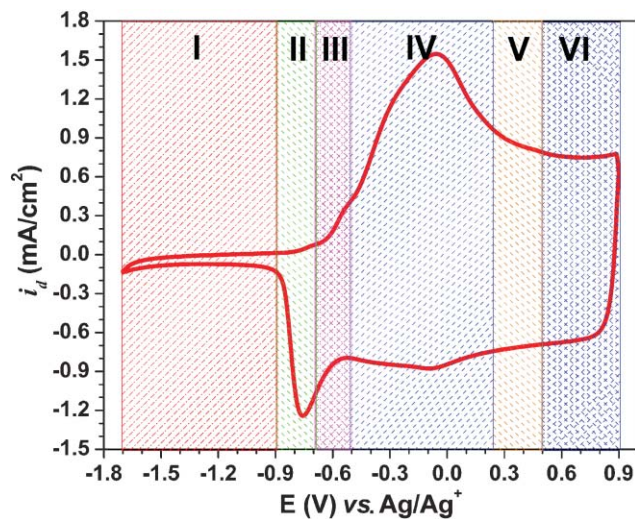

Fig. 4 Cyclic voltammogram of PEDOT film in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile (MeCN). Scan rate: 100 mV s^{-1}.

where the polymer backbone is destroyed, it loses its reversibility in terms of both electrochemistry and optoelectrochemistry.[21,48,49] Thus, it is important to know suitable potential windows for optical changes in polymeric electrochromics. For example, 92% of the total optical contrast was achieved in a potential window of only 0.75 V for PEDOT films. Exposure of the polymer film to unnecessarily high or low potentials may cause defects on the polymer backbone resulting in loss of optical properties.

Polymeric electrochromic devices and colour mixing

Having many oxidation steps between the neutral and oxidized forms of polymers, different colours obtained at these potential steps and recognition of these colours with the applied potentials opens new fields of application for polymeric electrochromics. Displays are probably the most important application in this manner. Since the three additive primary colours have been completed and we have demonstrated that at least 20 different tones of the same colour could be obtained from a single polymer, construction of a dual polymeric electrochromic device that uses two different conducting polymers can produce at least 400 different colours. This number can basically be reached by using 20 different oxidation states of each polymer that produces 20 different colours. A face-to-face combination of these polymers in a dual polymeric electrochromic device[19] produces a mixture of these colours. Since each polymer has 20 colours, multiplication of the numbers of possible colour tones of each polymer makes 400 different colours in this device. A schematic representation of a dual polymeric electrochromic device is presented in Fig. 5, where two ITO-coated glass slides were covered with conducting polymeric electrochromic layers as active materials. Then, a sandwich device was prepared by a face-to-face placing of the polymer-coated ITO slides. An electrolyte layer is applied between the two polymeric electrochromic layers, which can be a gel electrolyte, an ionic liquid or any electrolyte solution.

In principle, any two polymeric electrochromics can be used in a dual polymeric electrochromic device. However, use of
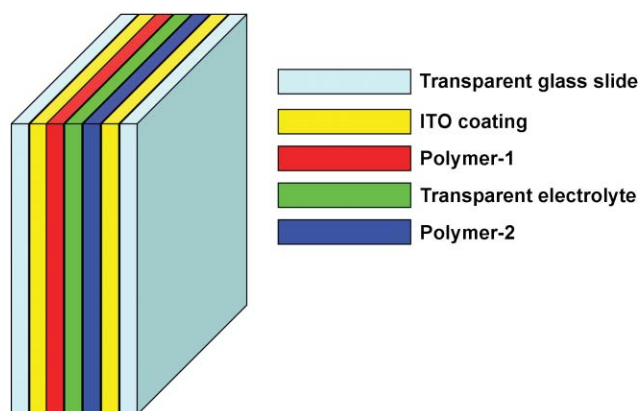
polymers reflecting additive (RGB) or subtractive (CMY) primary colours has an advantage. Since the locations of these colours in the CIE colour space are far enough apart, as shown in Fig. 2, possible interference can be prevented and more colours can be produced from their mixtures. As was explained in the calculation above, when conjugated polymers with the three additive primary colours (RGB) or subtractive primary colours (CMY) are used for colour mixing in a dual polymeric electrochromic device, at least 400 different colour tones can be obtained from the mixture of any two of these colours. This makes more than 1200 different shades of colours in total for the mixture of three polymers. This number is very promising for the application of these materials in display technologies and can also be increased very easily by using smaller potential variations for the switching of polymer films.

Fig. 6 represents an example of mixing red and blue coloured polymers in neutral and oxidized states. In this example, polymers **1** and **3** were first deposited on ITO-coated glass slides from an electrolyte solution containing their monomers. Then, polymer-coated ITO slides were patterned by removing polymer films from some parts, followed by a face-to-face insertion in a quartz UV-visible cuvette containing a monomer free electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (MeCN). Platinum and silver wire electrodes were used to control the oxidation potentials of the polymers. The three rows a, b and c represent the colours obtained from a mixture of polymers **1** and **3**, polymer **1** (red), and polymer **3** (blue), respectively. In column I, both polymers were in their neutral form; in II, polymer **1** was neutral and polymer **3** was in its oxidized state. In III, polymer **1** was oxidized and polymer **3** was neutral. Polymers **1** and **3** were both in their oxidized states in IV. The polymers **1–2**, and **2–3** were also matched in a similar way. Matching of the RGB coloured polymers in similar devices to that shown in Fig. 6 and the colours obtained from their mixtures at two oxidation states (neutral and oxidized) are presented in Fig. 7. Polymers **1** and **2**, in their neutral states, reflect red and green colours, respectively. The mixture of these two colours produces a very dark brown colour. When polymer **2** was oxidized, its colour changed from green to transmissive brown and mixing this colour with the red (neutral **1**) produced a reddish-brown colour. The oxidized

Fig. 5 Schematic representation of a dual polymeric electrochromic device. Polymer-1 and polymer-2 layers should be any two of the RGB coloured polymers. The transparent electrolyte can be a gel electrolyte, an ionic liquid or any electrolyte solution.
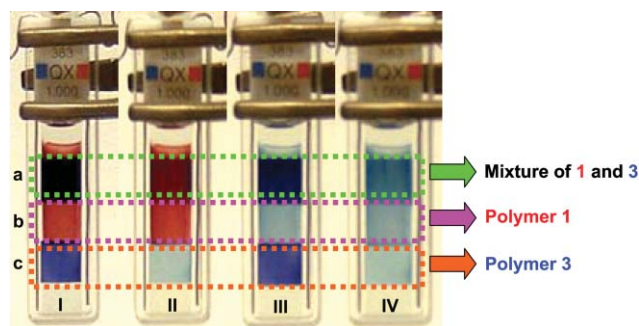

Fig. 6 Mixing patterned polymer layers on ITO-coated glass slides. The top layer (a) shows the colour mixtures obtained from polymers **1** and **3**, the middle layer (b) presents the red coloured polymer **1** in the neutral and oxidized states and the bottom layer (c) presents the blue coloured polymer **3** in the neutral and oxidized states.

Fig. 7 Different colours obtained when polymers reflecting additive primary colours (RGB) are mixed at the neutral (n) and oxidized (o) states. P3MeTh (**1**), PDDTP (**2**), and PEDOT (**3**) were used as red, green and blue coloured polymers, respectively.

state of **1** gives a sky blue colour, which gives a dark green colour when mixed with neutral **2**. When oxidized states of **1** and **2** are mixed, a grey-brown colour is obtained. A combination of **1** and **3**, and **2** and **3**, similarly, produces different colours at different oxidation states as shown in Fig. 7.

It is important to note that colour is a matter of perception and subjective interpretation. So that it may change from one person to another. Several factors affect colour perception, such as light source differences (sunlight, fluorescent light, incandescent light), observer differences (the sensitivity of each human eye is slightly different), size differences (colour covering large areas tends to appear brighter and more vivid than colour covering a smaller area), background differences (an object placed in front of a bright background looks duller than in front of a dark background) and directional differences (illumination or viewing angle). When studying the colour, its hue will vary depending on the illumination and its surrounding. Illumination changes the hue because colour is a light. Colour is the product of wavelengths that are either absorbed or reflected by the surface of an object being strongly illuminated. The hue appears to alter according to a colour's surroundings as the retina is affected by these wavelengths and the stimuli are communicated to the cortex, that part of the brain that enables us to distinguish one shade from another.

Other RGB coloured polymers and enhancement of electrochromic properties

The polymers presented in Fig. 7 are not the only examples of RGB reflecting polymeric electrochromics. To produce red colour a high band gap polymer with an absorption maximum at 500 nm is required. Poly(thiophene), poly(3-alkylthiophene)s, poly[2-methoxy-5-(2′-ethylhexyloxy)paraphenylene vinylene] and poly(3,4-ethylenedioxypyrrole) are some examples of other red reflecting polymeric electrochromics in their neutral states. All these polymers have band gaps higher than 2.0 eV. For a blue coloured polymer, a relatively low band gap is required. This time the polymer should have an absorption maximum at wavelengths above 600 nm and

should not absorb at shorter wavelengths. Poly(3,4-ethylene-dioxythiophene), poly(3,4-propylenedioxythiophene), poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine), poly(3,3-diethyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine) and poly(3,3-dibenzyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine) are very good examples of blue coloured polymeric electrochromics. Reflecting a green colour is more complicated as previously stated, because both red and blue colours should be absorbed to reflect a green colour. So far, several polymers have shown spectra that are good candidates for green coloured polymeric electrochromics as well as polymer **1**.[18–20,47] Other candidates are poly{5,7-bis[3,4-(ethylenedioxy)thien-2-yl]thieno[3,4-b]pyrazine},[50] poly(2,3-diphenyl-5,7-dithiophen-2-yl-thieno[3,4-b]pyrazine)[51] and poly{5,8-bis(3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylpyrido[3,4-b]pyrazine}.[25,52] Examining the structures of these polymers, they all contain a thieno-pyrazine ring fused

Table 1 Some examples of polymers reflecting RGB colours. *Red*: poly(3-alkylthiophene) (**1**), poly(thiophene) (**1a**), poly[2-methoxy-5-(2'-ethylhexyloxy)paraphenylene vinylene] (**1b**), poly(3,4-ethylenedioxy-pyrrole) (**1c**); *Green*: poly{2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine} (**2**), poly(2,3-diphenyl-5,7-dithiophen-2-yl-thieno[3,4-b]pyrazine) (**2a**), poly{5,8-bis(3-dihydrothieno[3,4-b][1,4]dioxin-5yl)-2,3-diphenylpyrido[3,4-b]pyrazine} (**2b**), poly{5,7-bis[3,4-(ethylenedioxy)thien-2-yl]thieno[3,4-b]pyrazine} (**2c**); *Blue*: poly(3,4-ethylenedioxythiophene) (**3**), poly(benzo[c]thiophene) (**3a**), poly(3,4-propylenedioxythiophene) (**3b**), poly(3,3-dialkyl-3,4-dihydro-2H-thieno[3,4-b]dioxepine) (**3c**)
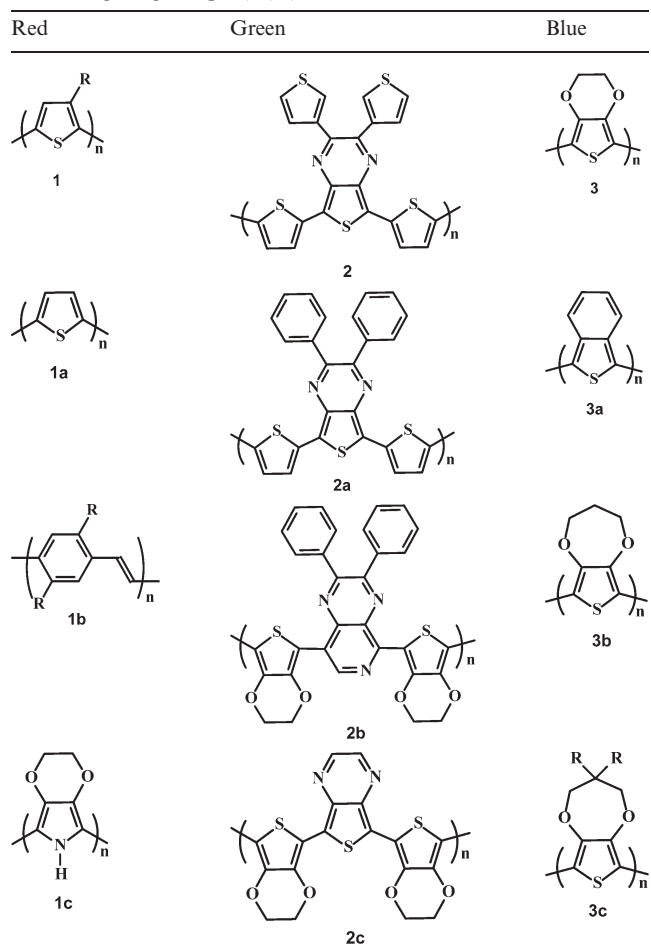
Red	Green	Blue

to the thiophene or pyridine rings. Four structures for each of red, green and blue reflecting polymers are given in Table 1 as examples. It is very important to note that the polymer structures shown in Table 1, are not the final structures and some of them still need to be improved in the aspects of colour saturation, response time, coloration efficiency, shorter synthesis procedures, *etc*. PEDOT is an excellent example to examine in terms of enhancements in electrochromic properties, which have been investigated by Reynolds' group.[31] They, first, changed the ethylenedioxy substitution at the 3 and 4 positions of thiophene (PEDOT) to propylenedioxy (PProDOT), and then to butylenedioxy (PBuDOT), resulting in an improvement in the optical spectrum and the response time. PProDOT gave a sharper spectrum at almost the same wavelength as PEDOT. Then, addition of other functional groups, such as short or long alkyl chains, sulfonated alkyl groups and dibenzyl groups, reduced the switching time of the polymer from 2.2 to 0.23 seconds, improved the optical contrast from *ca.* 45% to 75% and made the polymer processable in organic solvents and water.[53] Finally, both Bauerle[54] and Reynolds[55] independently demonstrated efficient routes for the synthesis of these monomers by reducing the number of steps in the synthetic procedures. With these improvements, we believe, the blue leg of the RGB colours is ready for industrial applications. But, on the other hand, both the red and the green legs of the additive colour space are still waiting for similar improvements.

RGB and CMYK colour mixings

Colour mixing in display technologies works using the principle of colour as a light and involves mixing RGB colours in varying intensities to create a multitude of colours.[56] The intensity of light ranges from 0 to 256, controlling the creation of varied values of hue and chroma. Thus, RGB colours can be combined in 256 possible intensities each to give a maximum of 16 777 216 (256^3) possible colour combinations. When all RGB colours are displayed at 0 or 256, the result is black or white, respectively. Similarly, subtractive primary colours (CMY) can also be mixed to produce new colours. Mixing these three colours produces black, absence of light, which is also included in the colour mixing systems, and usually subtractive primary colours are represented as CMYK where "K" stands for "black". The colour mixing situation is not different in the subtractive colour space. Again, different shades of colour can be produced by mixing yellow (Y), cyan (C) and magenta (M) colours. For instance, a mixture of C, M and Y with the percentages 12, 40 and 20, respectively, produces a pink colour. A mixture of 75% C and 85% M gives a purple colour. A detailed table of the colours that can be produced using CMYK colours is given in Fig. 8. These percentages can be tuned sensitively with the applied voltages in polymeric electrochromics as the subtractive colour space is completed, in which polymers switch from their coloured states to the white point as shown in Fig. 2.

Conclusion

In conclusion, the door to a new era for polymeric electrochromics was opened with the discovery of the first green polymeric electrochromic.[18] Using other polymers reflecting red and blue colours (*i.e.*, P3MeTh and PEDOT, respectively) completed the three legs of the additive primary colour space, RGB. These polymers switch from the RGB colours to their transmissive colours upon oxidation. Between their two extreme states of oxidation (neutral and oxidized), they produce more than 20 different tones of the same colour.
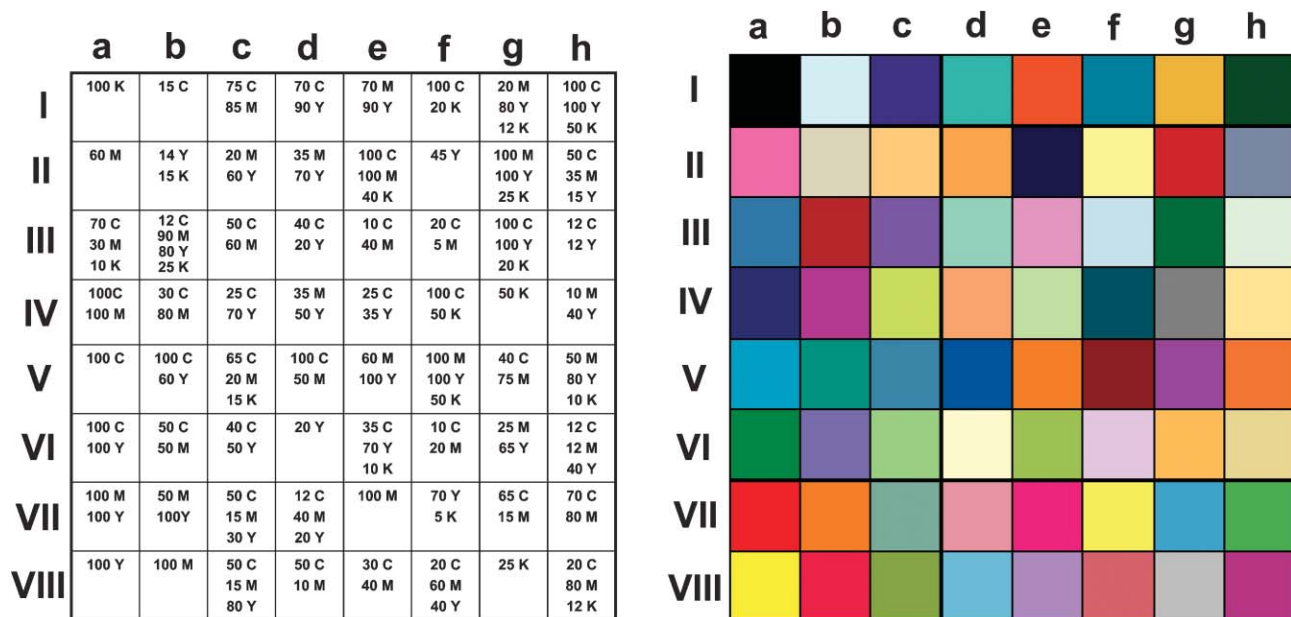
	a	b	c	d	e	f	g	h
I	100 K	15 C	75 C 85 M	70 C 90 Y	70 M 90 Y	100 C	20 M 80 Y 12 K	100 C 100 Y 50 K
II	60 M	14 Y 15 K	20 M 60 Y	35 M 70 Y	100 C 100 M 40 K	45 Y	100 M 100 Y 25 K	50 C 35 M 15 Y
III	70 C 30 M 10 K	12 C 90 M 80 Y 25 K	50 C 60 M	40 C 20 Y	10 C 40 M	20 C 5 M	100 C 100 Y 20 K	12 C 12 Y
IV	100 C 100 M	30 C 80 M	25 C 70 Y	35 M 50 Y	25 C 35 Y	100 C 50 K	50 K	10 M 40 Y
V	100 C	100 C 60 Y	65 C 20 M 15 K	100 C 50 M	60 M 100 Y	100 M 100 Y 50 K	40 C 75 M	50 M 80 Y 10 K
VI	100 C 100 Y	50 C 50 M	40 C 50 Y	20 Y	35 C 70 Y 10 K	10 C 20 M	25 M 65 Y	12 C 12 M 40 Y
VII	100 M 100 Y	50 M 100Y	50 C 15 M 30 Y	12 C 40 M 20 Y	100 M	70 Y 5 K	65 C 15 M	70 C 80 M
VIII	100 Y	100 M	50 C 15 M 80 Y	50 C 10 M	30 C 40 M	20 C 60 M 40 Y	25 K	20 C 80 M 12 K

Fig. 8 An example of colour mixing in the subtractive colour system, adopted from ref. 56 (Garo, Laurie and Bo King, 1998. Cartography Laboratory, Department of Geography & Earth Sciences, University of North Carolina at Charlotte). Mixing different amounts of CMYK colours (left) produces different colours (right). C: cyan, M: magenta, Y: yellow, K: black.

The ease of controlling colour with the applied potentials, low power requirements for switching and high stability are some of the additional advantages of these materials for applications in electrochromics. Mixing any two of the RGB coloured polymers in a dual polymeric electrochromic device produces at least 400 shades of colour for each combination of the RGB polymers (R–G, R–B and G–B), making more than 1200 colours in total. Similarly, subtractive primary colours, CMY, are waiting for completion. This will definitely help to bring polymeric electrochromics to daily life. The enhancements achieved in blue coloured polymers set a very good example for the improvement of optical properties of other polymeric electrochromics. Sharper spectra in the neutral and more transmissive colours in the oxidized form of RGB coloured polymers, completion of the subtractive primary colours, higher optical contrasts in the visible region, reduction of the numbers of synthetic steps in the production of both monomers and polymers, and improvements in the switching time are some examples of forthcoming researches in polymeric electrochromics.

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