

Solution-processable triarylamine-based electroactive high performance polymers for anodically electrochromic applications

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This review focused on high-performance polymers with anodically electrochromic triarylamine units built into main chains or as pendants. The main aim of the review is to present the most important and common trends regarding polymer synthesis from the point of view of the introduction of triarylamine moiety into polymer chains and to demonstrate how the polymer structures influence their properties, which leads them to be suitable for optoelectronic device construction. This review also covers a majority of the works in the recent decade involving the synthesis and characteristic evaluation of the resulting electrochromic polymers as well as their structural design by using the respective monomers.

1. Introduction

In today's world, life without polymers is unimaginable. Polymers have become major synthetic materials of the 21st century. High-performance polymers are the most desirable especially. The synthesis and development of high-performance polymers in the past thirty years have particularly drawn the attention of many polymer scientists and investigators. In general, these polymers possess excellent deformation resistance (physics) and

deterioration resistance (chemistry) at high temperatures over a long period of time. The quest for high-performance polymers began in the late 1950s to meet the demands for military, aerospace, machine-building, electronics, and many industrial applications.

Hill and Walker first pointed out that the incorporation of aromatic segments into a polymer generally results in a noticeable increase in its thermal stability.¹ For this reason, much of the research work has been directed toward aromatic compositions. Hence, high-performance polymers usually tend to contain more aromatic units in their structure. Several of these aromatic high-performance polymers have reached commercialization such as

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Guey-Sheng Liou

Guey-Sheng Liou received his PhD in 1993 under the supervision of Professor Yoshio Imai at the Tokyo Institute of Technology. He then worked as a researcher in the Union Chemical Laboratory, Industrial Technology and Research Institute, Taiwan. He joined I-Shou University and was promoted to professor in 2000. He moved to National Chi Nan University from 2001–2007. He is presently a professor of Institute of Polymer Science and Engineering, National Taiwan University. His research interests include the development of organic electrochromic materials, light-emitting aromatic polymers, thermal stable polymers for microelectronics and energy-related applications, and polymer-inorganic hybrid materials.

aromatic polyamides, polyimides, polyesters, polysulfones, and heterocyclic polymers (Scheme 1). Aromatic polyamides (aramids) and polyimides, such as DuPont's Kevlar fiber and Kapton film, have been well known for a long time and constantly attract much interest more than other high-performance polymers for their several useful properties such as excellent thermal and oxidative stability, high mechanical strength, low flammability, good chemical and radiation resistance.²

However, rigidity of the backbone and strong hydrogen bonding results in high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents.³ These properties make them difficult to process, thus restricting their technological applications. To overcome such a dilemma without sacrificing high thermal stability, introduction of bulky and packing-disruptive groups into the polymer backbone is a feasible approach;⁴ triphenylamine (TPA) derivatives provide an avenue. Since 2002, we have developed the synthesis of soluble aromatic polyimides and polyamides containing TPA units. Because of the incorporation of a bulky, propeller-shaped TPA structure along the polymer backbone, all the polymers were amorphous, showed good solubility in many aprotic solvents, good film-forming capability, and high thermal stability.⁵

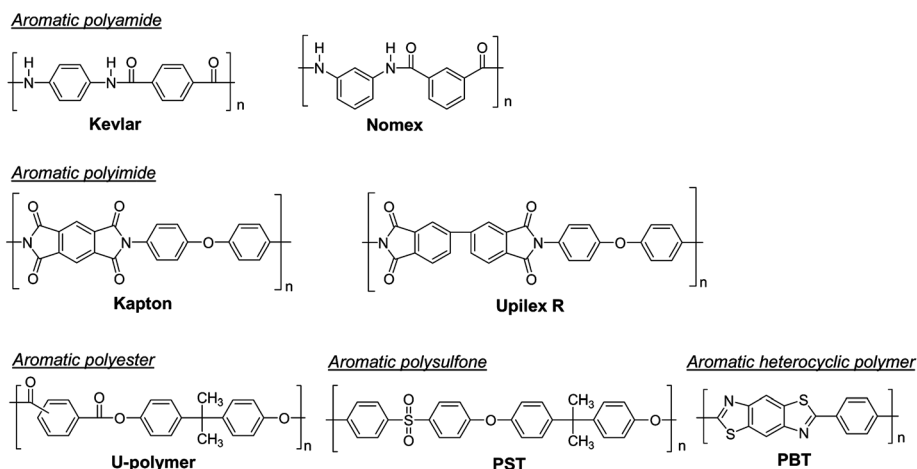
Triarylamine-containing materials are generally colorless unless they undergo some form of charge-transfer interaction with an electron-deficient acceptor species. By contrast, electron-rich triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, the synthesis and electrochromic (EC) behavior of triarylamine-based polymers have been reported in the literature.⁶ Electrochemical polymerization was usually utilized and high-quality oxidized polymer thin film can be formed directly onto electrode surfaces (Scheme 2 and Table 1).⁷ However, most of them were insoluble after deposition on the electrode surface which may hamper their applications for large area devices. Thus, other means were developed to obtain solution-processable EC polymers, such as the Suzuki–Miyaura cross-coupling reaction⁸ (Scheme 3 and Table 2), 2+2 cyclo-dimerization of trifluorovinyl ether⁹ (Scheme 4), and the oxidative coupling reaction¹⁰ (Scheme 5).

An electroactive species often exhibits new optical absorption bands in accompaniment with an electro-transfer or redox

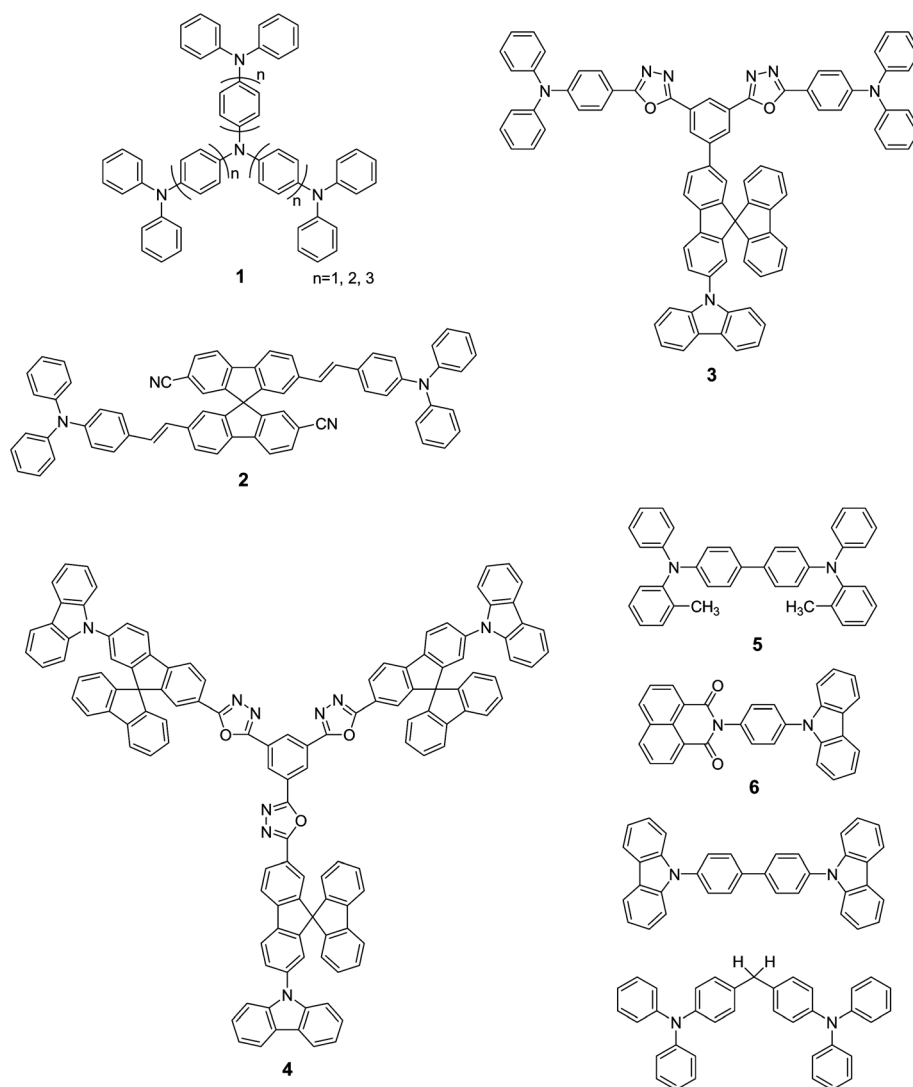
reaction in which it either gains or loses an electron; that is to say, it undergoes *reduction* or *oxidation*. Chemical species may be electrochemically switched between different colors, and the color change is commonly between a transparent ('bleached') state and a colored state, or between two colored states. Such coloration was first termed electrochromism by Platt in 1961.¹¹ Byker has discussed the historical development of electrochromism,¹² where more than two redox states are electrochemically accessible in a given electrolyte solution, and these EC materials may exhibit several colors and could be termed polyelectrochromic.

Whilst many types of chemical species exhibit electrochromism, only those with favorable EC performance parameters^{13a} are potentially useful in commercial applications. EC anti-glare car rear-view mirrors have already been commercialized, with other proposed applications of EC materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, glare-reduction systems for offices, and 'smart windows' for use in cars and in buildings.¹³ Of these, EC car rear-view mirrors have already achieved considerable commercial success. These safety devices prevent mirror-reflected glare which causes an 'after image' to stay on the eye's retina. Thus most applications require EC materials with a high contrast ratio, coloration efficiency (absorbance change/charge injected per unit area), cycle life, and write-erase efficiency (% of originally formed coloration that may be subsequently electro-bleached). Whereas displays need fast response times, by contrast 'smart windows' can tolerate response times of up to several minutes. Generally the advantages of polymeric EC materials that applied in EC devices can be summarized as following:

- (1) Low driving voltage (< 1.5 or 3.5 V)
- (2) Rapid response time [second (mirror)–minute (window)]
- (3) High color contrast (transmittance attenuation = $\Delta T > 30\%$)
- (4) Long cycle life (>10 yr for window, >3yr for mirror)
- (5) Environmental stability (electrochemical, thermal, & UV)
- (6) Low cost, easy processing
- (7) Multiple colors with the same material



Scheme 1



Scheme 2

Table 1 Colors of polymers derived from electropolymerization of arylamines

Polymer	Color transition			Ref.
	Neutral	1st ox.	2nd ox.	
1	Yellowish	Orange	Deep blue	7a
2	Pale yellow	Red	Blue	7b
3	Pale yellow	Orange	Blue	7c
4	Transparent	Green	Light blue	7d
5	Pale orange	Green	Blue	7e
6	Yellowish green	Dark green	Blue (reduction)	7f

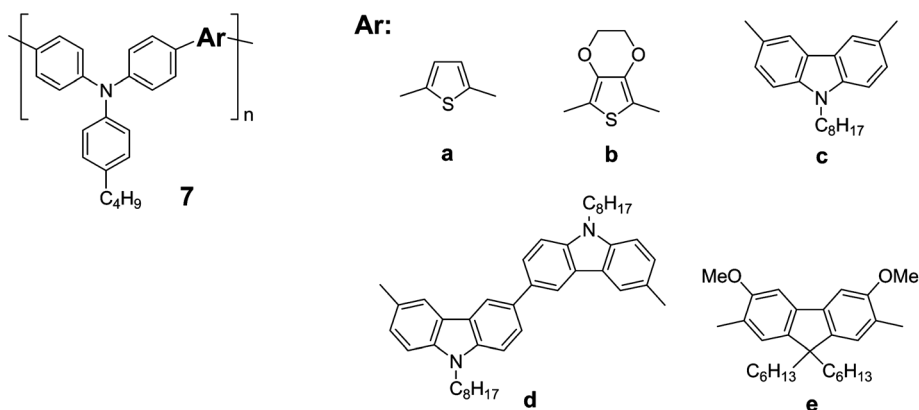
Electron-transfer (ET) interaction between electroactive species is one of the most fundamental processes in chemistry¹⁴ and biology.¹⁵ Thus, numerous investigations were devoted to the study of ET processes in real biological systems,¹⁶ in biomimetic model compounds,¹⁷ and in structurally simple and completely artificial low molecular weight systems.¹⁸ The aim was to understand ET processes in nature and to design the molecular wires for electronic communication.¹⁹ Since the

studies of mixed-valence compounds reported by Creutz and Taube,²⁰ simple inorganic derivatives were used as model systems to study the basic aspects of ET theories and check the applicability of Hush theory for interpreting intervalence charge transfer (IV-CT) absorption spectra.²¹ In 1967, Robin and Day²² classified mixed-valence compounds with two (or more) redox centers into three categories: (a) the redox centers are completely localized and behave as separate entities (class I), (b) intermediate coupling between the mixed valence centers exists (class II), and finally (c) class III derivatives where coupling is so strong that the system is completely delocalized and intermediate redox states have to be attributed to the redox centers.

2. Initiated triarylamine-based electrochromic polymers

2.1. Polyimides

Aromatic polyimides can be categorized as an important class of materials because of their many desirable characteristics and



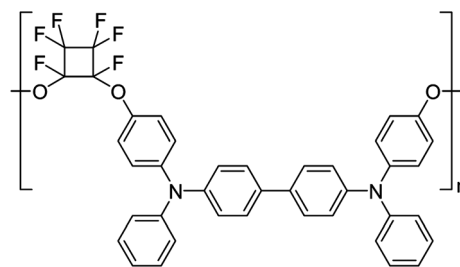
Scheme 3

often replace glass and metals in many industrial applications, especially in the semiconductor and electric packaging industry. The outstanding properties of aromatic polyimides come from their rigid backbones and strong intramolecular and intermolecular forces between the polymer chains due to the charge transfer complex formation between electron-donating (diamine moiety) and electron-accepting (dianhydride moiety) segments.

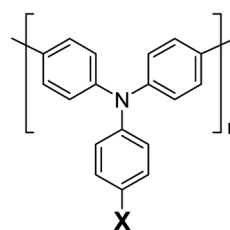
TPA based polyimides were first prepared in 1992 from 4,4'-diaminotriphenylamine and various tetracarboxylic dianhydrides by Imai *et al.* (Scheme 6).²³ These polymers were soluble in many polar solvents and showed useful levels of thermal stability associated with high glass-transition temperatures (T_g) (287–331 °C) and high char yields.

Since 2005, our group prepared the first EC aromatic polyimides with pendent TPA units from the newly synthesized diamine, *N,N*-bis(4-aminophenyl)-*N',N'*-diphenyl-1,4-phenylenediamine, and various tetracarboxylic dianhydrides by either a one-step or a conventional two-step polymerization process (Fig. 1).²⁴ All the polyimides were amorphous showing high solubility in many organic solvents, and could be solution cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with relatively high glass transition temperatures. The polyimide films exhibited two reversible oxidation redox couples and revealed good stability of EC characteristics with distinct color change from pale yellowish to green and then blue during oxidation procedure.

In the following years, our group^{25a,25b} and Hsiao *et al.*^{25c–25h} continuously reported the synthesis of high-performance polyimides carrying the TPA or other triarylamine derivatives as electroactive functional moieties (Scheme 7). All the polyimides



Scheme 4



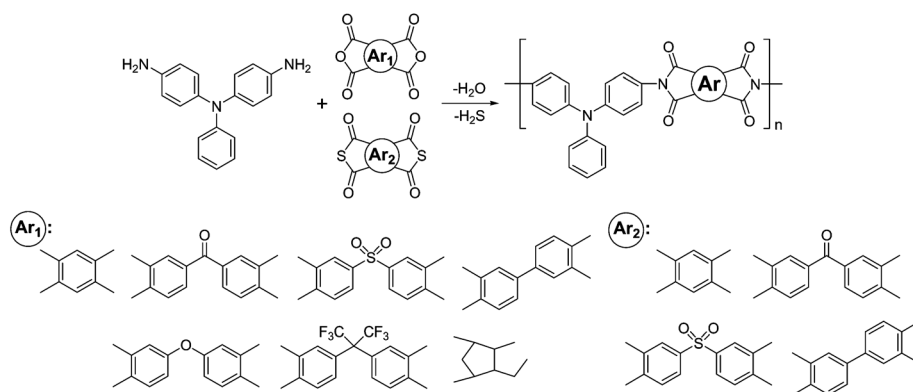
X: OMe, CN, NO₂

Scheme 5

were highly solution-processable and exhibited excellent thermal stability with high T_g s. The polyimide films showed excellent adhesion with ITO-coated glass electrode and good electrochemical stability, and also revealed EC characteristics when scanning potentials positively. Thus, the TPA-based polyimides could be good candidates as anodic EC materials because of their proper oxidation potentials, electrochemical stability, and thin film forming ability.

Table 2 Colors and oxidation onset potential of polymers

Polymer		7a	7b	7c	7d	7e
Color transition	Neutral Oxidized	Yellow Green	Yellow Green	Colorless Khaki	Colorless Khaki	Pale green Reddish-brown
E_{onset} (V vs. SCE)		1.19	0.95	1.16	1.16	1.19



Scheme 6

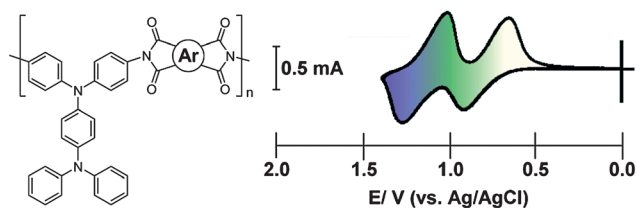
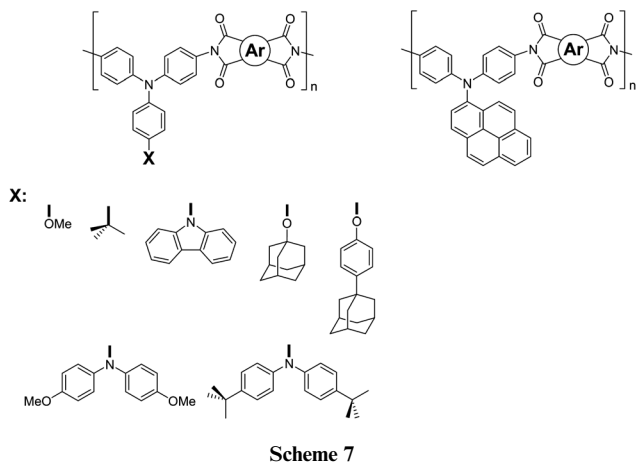


Fig. 1 Cyclic voltammetric diagrams of polyimide and its electrochromic behavior. Reprinted with permission from ref. 24, Copyright 2011 American Chemical Society.



Scheme 7

2.2. Polyamides

It is well known that the aromatic polyamides as microelectronic materials have attracted great interest due to their outstanding thermal and mechanical resistance.² Incorporation of packing-disruptive TPA units into polyamides not only preserves high thermal stability, glass transition temperature, and the solubility for enhancing the film-forming ability which is beneficial for their fabrication of large-area thin-film EC devices but also provides the electroactive center to facilitate both processing and EC applications.

Polyamides containing TPA groups were first prepared in 1990 from 4,4'-diaminotriphenylamine and various dicarboxylic acids by Imai *et al.* via the phosphorylation polyamidation. (Scheme 8).²⁶

Since 2005, our group^{27a–27f} and Hsiao *et al.*^{25c–25e,27g–27j} developed several TPA-containing EC polyamides with interesting color transitions (Scheme 9). These polymers were readily soluble in many organic solvents and showed useful levels of thermal stability associated with high glass-transition temperatures and high char yields. Some of the polymer films exhibited reversible electrochemical oxidation with high contrast ratio in the visible range or near-infrared (NIR) region, high coloration efficiency (CE), low switching time, and the high stability for long-term EC operation.

2.3. Poly(amide-imide)s

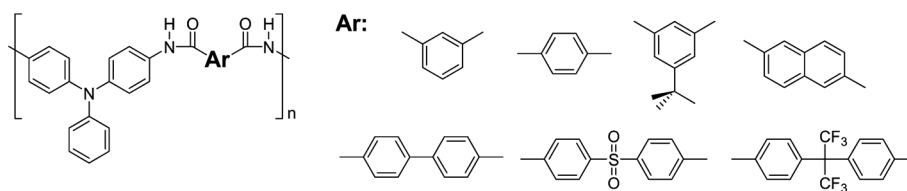
The intractable characteristic of aromatic polyimides is major problem as a result of high melting points and insolubility. To overcome this drawback, copolymerization is an effective approach and various copolyimides have been developed. Recently, poly(amide-imide)s have been developed as an alternative material offering a compromise between excellent thermal stability and processability.

We also reported aromatic poly(amide-imide)s having *para*-methoxy substituent, *para*-*t*-butyl substituent, pendent triphenylamine and *N*-carbazolylphenyl units from the phosphorylation polyamidation of the synthesized diamine with imide ring-preformed dicarboxylic acids²⁸ (Scheme 10). All the polymers are highly soluble in polar organic solvents. Flexible, tough, and amorphous films of these poly(amide-imide)s could be obtained by solution casting, and exhibited reversible electrochemical oxidation redox couples, good EC stability, and high contrast of optical transmittance change.

3. Development of triarylamine-based electrochromic polymers

3.1. Introduction of protecting groups

For the requirements of practical applications, long-term stability, rapid redox switching, large changes in transmittance (large $\Delta\%T$) between their bleached and colored states, and high coloration efficiency are crucial factors for EC materials.²⁹ As an EC functional moiety, the TPA unit has two basic properties: (1) the easy oxidizability of the nitrogen center and (2) its hole-transporting ability via the radical cation species. The anodic oxidation pathways of TPA were well studied.³⁰ The electrogenerated cation



Scheme 8

radical of TPA⁺ is not stable and could form tetraphenylbenzidine (TPB) by tail to tail coupling. When the phenyl groups were incorporated by electron-donating substituents at the *para*-position of TPA (Fig. 2),^{27a} the electrochemical oxidative coupling reactions could be greatly prevented due to affording stable cationic radicals and lowering the oxidation potentials of the resulting electroactive polymers (Scheme 11).^{27d,27f,31}

3.2. Enhancement of electrochromic-coloring stages

The arylamine/TPA containing electrochromic polymers (ECPs) with interesting color transitions reported by our group can be differentiated on the basis of method of increasing coloring stages. The first class spans materials polymerized from two electroactive monomers with very similar structures (*e.g.*, polyamides prepared by diamines and diacids) (Scheme 12 and Scheme 13).^{32,28d–28f} The derived polyamides containing two or more TPA units have multiple redox stages to tune and produce multiple colors.

The second class includes the further introduction of electroactive units by chemical modification on the end functional groups of EC hyperbranched polymers (Fig. 3).³³ In addition to the excellent solubility for processing the resulting A₂B-type

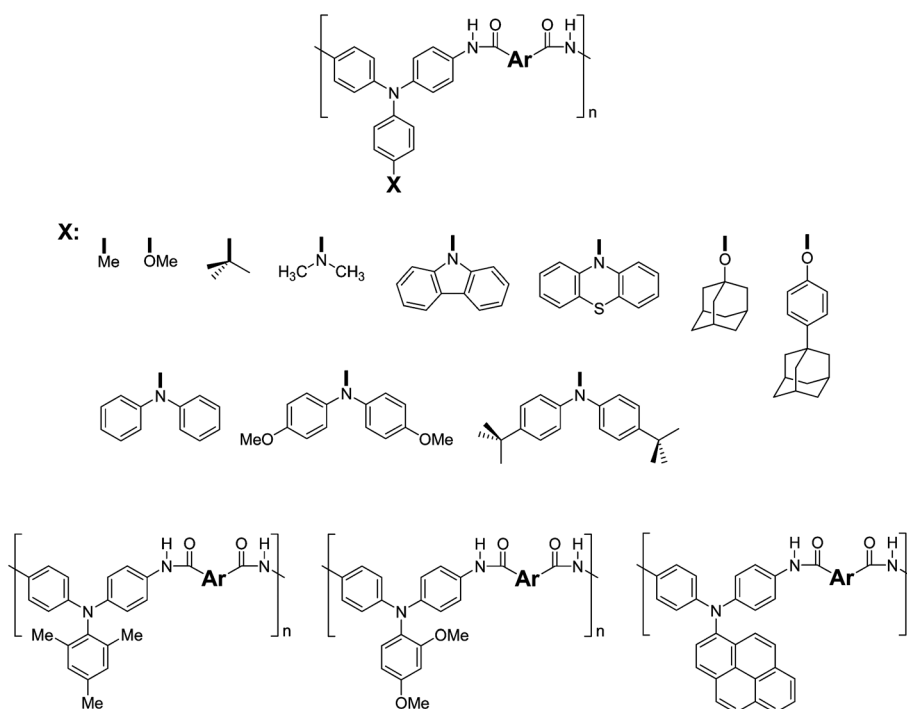
hyperbranched polyamide could be end-capped by incorporating another *para*-methoxy-substituted TPA functional groups to produce different EC characteristics.

The third class is represented by increasing the electroactive sites into the target monomers by multi-step synthetic procedures (Fig. 4).^{27a,34}

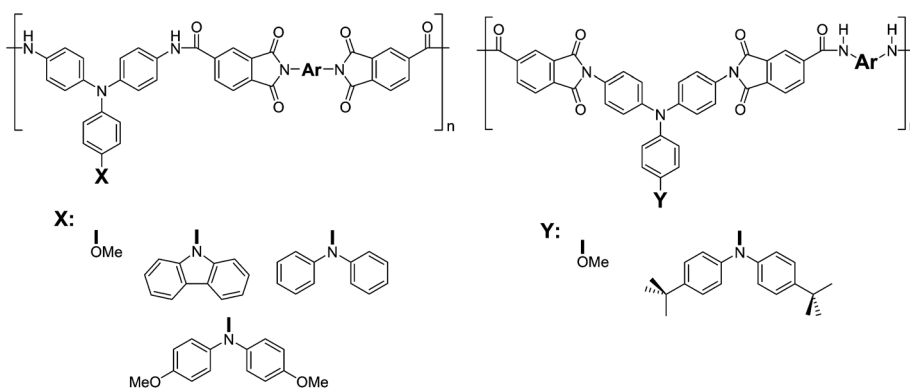
Finally, by random copolymerization³⁵ of *N,N,N',N'*-tetraphenylbenzidine (TPB) and *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine (TPPA)-based diamine monomers, the resulting copolymer could exhibit an extensive absorption ranging of 400–750 nm required for a black electrochromism with multicolor electrochromism (Fig. 5). This simple band-merging concept is an effective approach to generate electroactive polymers which are colorless in neutral state but show broad and homogeneous absorption bandwidths extending over the entire visible spectrum and could be successfully achieved during different oxidation stages, that will span numerous applications including EC windows and displays.

3.3. Bridged triarylamine-based polymers with IV-CT behavior

According to Robin and Day,²² the TPPA cation radical has been reported as a symmetrical delocalized class III structure



Scheme 9



Scheme 10

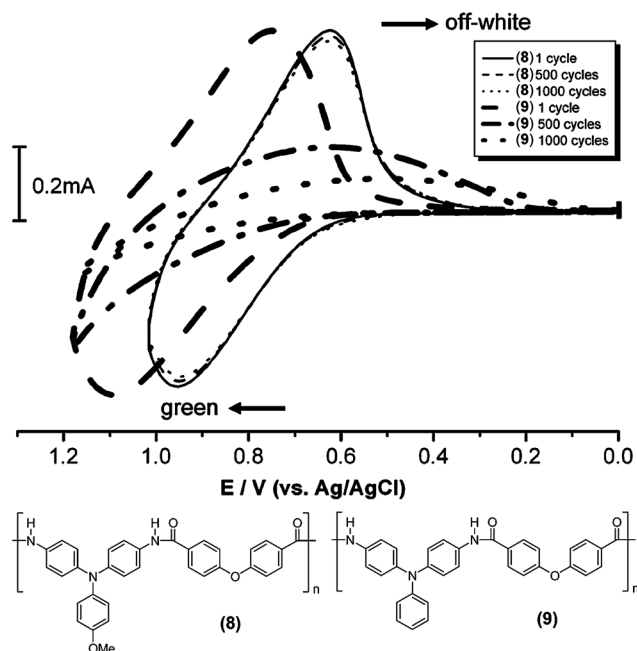
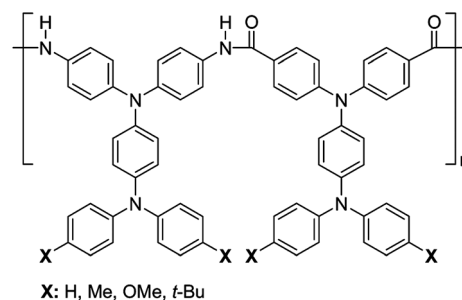
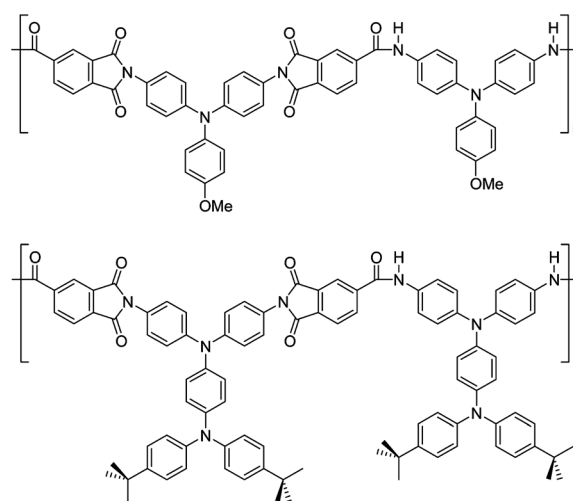


Fig. 2 Cyclic voltammograms of polyamides **8** and **9**. Reprinted with permission from ref. 27a, Copyright 2011 The Royal Society of Chemistry.

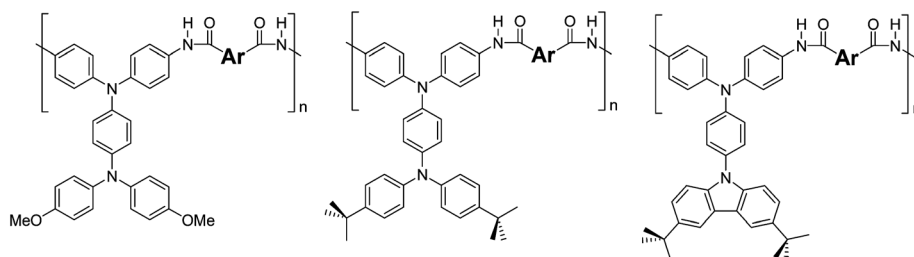
with a strong electronic coupling while the TPB cation radical was demonstrated as a class II structure with a weakly electronic coupling, both leading IV-CT absorption bands in the NIR region.³⁶ These results made the aryldiamine-containing molecule



Scheme 12



Scheme 13



Scheme 11

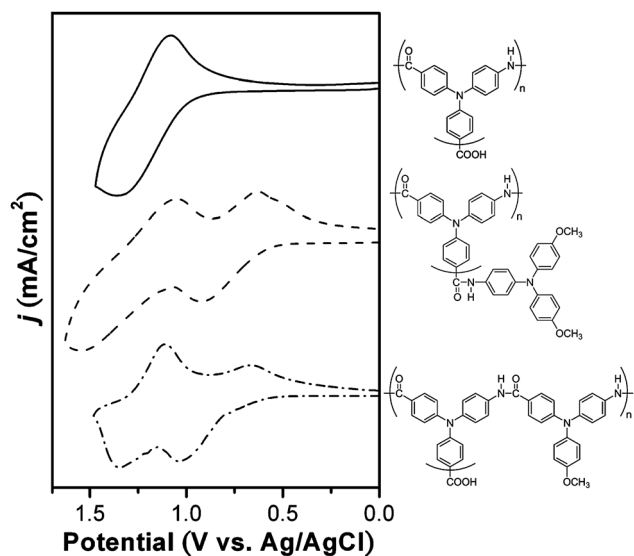


Fig. 3 Cyclic voltammetric diagrams of the hyperbranched polyamide films. Reprinted with permission from ref. 33, Copyright 2011 The Royal Society of Chemistry.

an interesting anodic EC system for NIR applications. In our laboratory, we have developed systematically about TPPA and TPB-containing aromatic polyamides,^{34a,35} which revealed

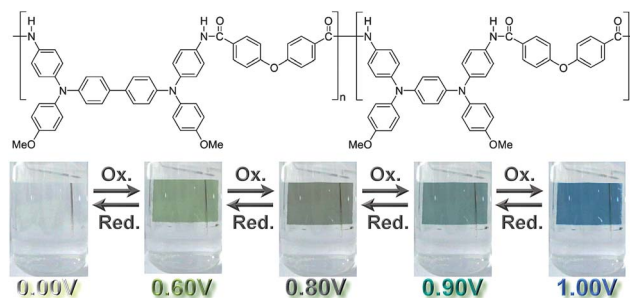


Fig. 5 Chemical structure of the copolyamide and its electrochromism at the different applied potential. Reprinted with permission from ref. 35, Copyright 2011 The Royal Society of Chemistry.

typical class III and II transition in MV systems, respectively. Moreover, the MV class I character and behavior could be obtained in the resultant electroactive polymers by using the ether-linkage as a block and definitely isolated the two redox centers (Scheme 14).³⁷ By the introduction of ether-linkage into bis(triphenylamine)ether (TPAO) unit, the resulting polymers containing two separated redox centers revealed independent electrochemical behavior, and two electrons within TPAO moiety are simultaneously removed to form two radical cations without intramolecular electron transfer. The mixed-valence I/II/III transition and electrochemistry of the synthesized materials

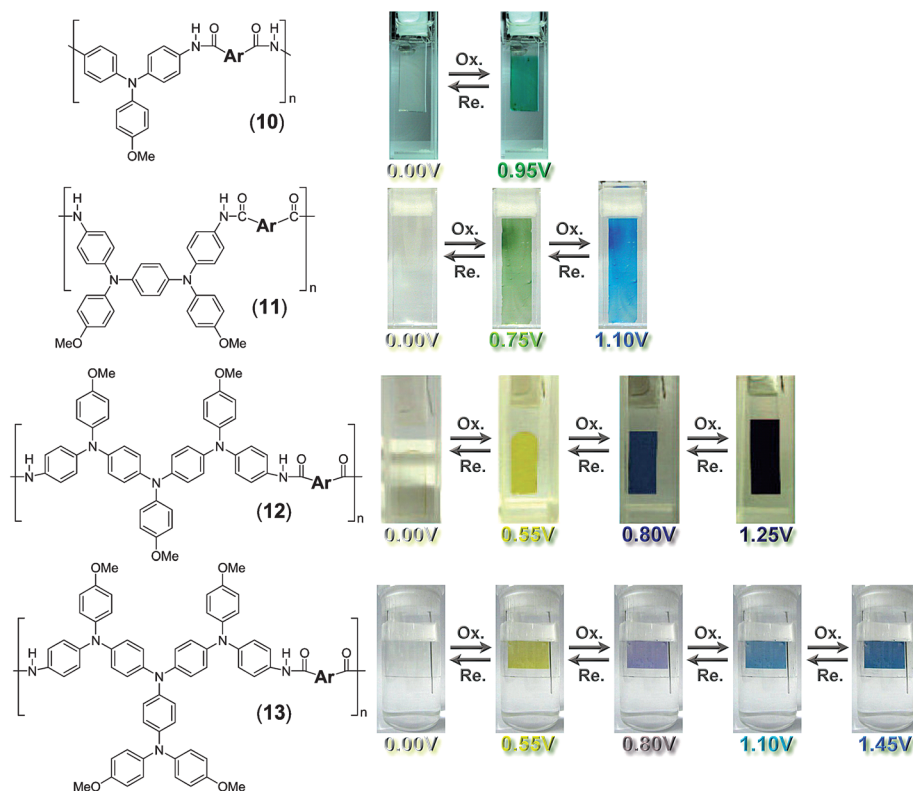
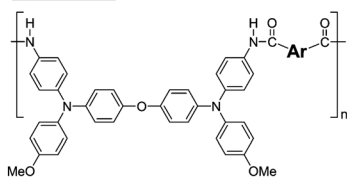
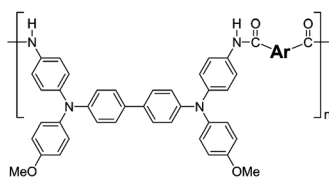
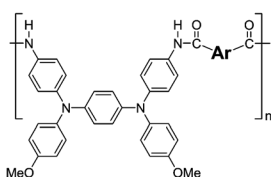


Fig. 4 Chemical structure of the polyamides and their electrochromism at the different applied potential. (10) Reprinted with permission from ref. 27a, Copyright 2011 The Royal Society of Chemistry; (11) Reprinted with permission from ref. 34a, Copyright 2011 American Chemical Society; (12) Reprinted with permission from ref. 34b, Copyright 2011 American Chemical Society; (13) Reprinted with permission from ref. 34c, Copyright 2011 American Chemical Society.

MV Class I**MV Class II****MV Class III**

Scheme 14

were investigated for the bridged triarylamine system with various N–N distances and intramolecular electron transfer capability.

4. Conclusions

This review covers a majority of the works in the recent decade involving the synthesis and characteristic evaluation of the resulting triarylamine-based EC polymers as well as their structural design by using the respective monomers. The solution-processable high-performance polymers utilizing the triarylamine unit as an EC functional moiety reveal interesting color transitions with good EC reversibility in the visible region or NIR range, and could be differentiated on the basis of method of increasing coloring stages. The first class spans materials polymerized from two electroactive monomers with similar structures, second class includes the further introduction of electroactive units by chemical modification on the end functional groups of EC hyperbranched polymers. The third class is represented by increasing the electroactive sites into the target monomers by multi-step procedure approaches. Finally, the simple band-merging concept of copolymerization also is a very effective approach to generate electroactive polymers which are colorless in the neutral state but exhibit extensive absorption ranging of 400–750 nm required for a black electrochromism that will span numerous applications including EC windows and displays. Moreover, the mixed-valence I/II/III transition and electrochemistry of the synthesized materials were also investigated for the bridged triarylamine systems.

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