

Styrene-maleic anhydride copolymer (SMA) derived high-performance triarylamine-containing electrochromic materials¹

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Abstract

A facile approach is employed to produce thermosets of styrene-maleic anhydride copolymers (SMA) containing various triarylamine moieties. The impact of counter-ion diffusion kinetics during the electrochemical reaction is examined by applying ion exchange modification. The commercial SMA is reacted with three arylamine-based diamine monomers, **3Ph**, **5Ph**, and **7Ph**, to form colorless thermoset polymer films. The triethylamine (Et₃N) is also utilized to possess the ion exchange method after forming polyamic acid (PAA) to improve counter-ion migration. Enlarging the porous size and triethylammonium-containing in the polymer matrix leads to synergistic enhancements in the diffusion dynamics of the counter-ion and the electrochromic properties.

Introduction

Electrochromic (EC) materials reversibly change color or optical properties in response to an applied electrical voltage or current. A desirable EC polymer should manifest some attractive features, including high color contrast, fast response time, swift coloring speed, significant coloration efficiency, low oxidation voltage, excellent stability, and a wide range of available colors. Recent research has demonstrated that cross-linking structures could facilitate electrolyte counterion diffusion by increasing the interchain distance within polymers.

A facile and industrially practical approach to generating cross-linking structures of redox-active polymer films with different interchain distances is presented in this work to elucidate the relationship between interchain distance and EC properties using a series of triarylamine-based diamine cross-linkers to couple with SMA, as shown in **Figure 1**. The resulting thermoset polymers exhibited enlarged interchain distance and accelerated diffusion of the electrolyte counterion via controlling the size of triarylamine moieties. Furthermore, the ionization approach was also feasible to facilitate efficient ion transport, reduce resistance, and improve overall electrochemical efficiency. Consequently, the ionization method was applied by using triethylamine (Et₃N) at the polyamic acid (PAA) stage to form carboxylate/triethylammonium complexes within the polymer matrix, which could substantiate faster diffusivity and enhance the EC switching response capability. Furthermore, the relationship between the interchain distance, diffusion dynamics, and electrochemical behaviors related to these two approaches was investigated systematically.

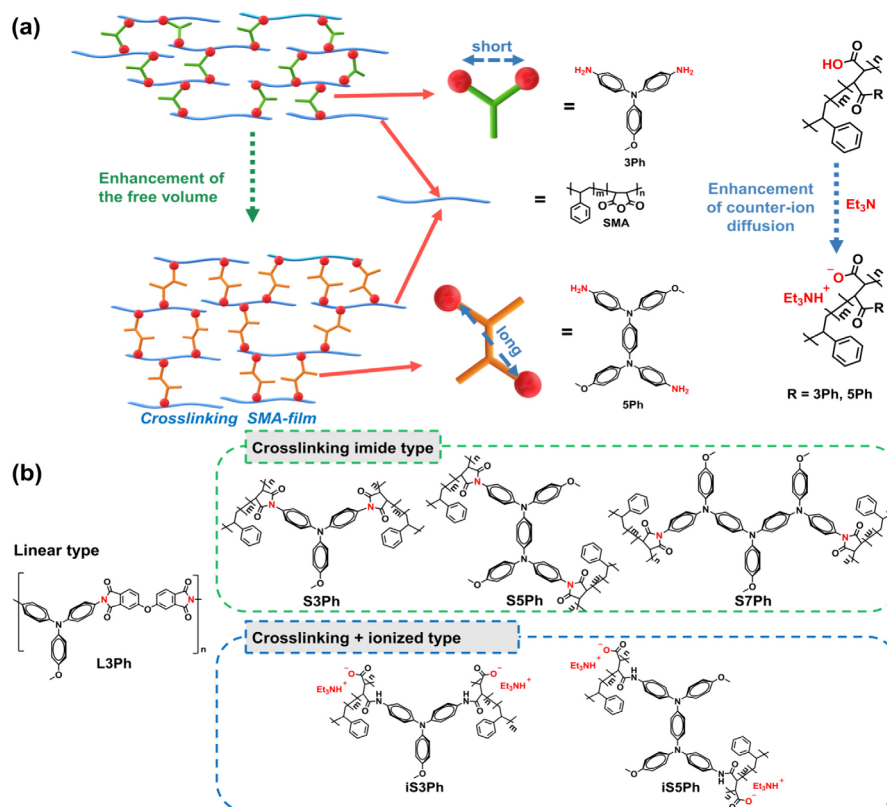


Figure 1. (a) Schematic presentation of cross-linking structures of SMA with different triarylamine linkers and (b) the target studied polymer structures in this work.

Experimental

Synthesis of SMA-Based-Cross-Linking Polymers. The synthesis of polymers S3Ph is used as an example to illustrate the general synthetic route. The typical procedure was as follows: a mixture of 3Ph (0.1644 g, 0.125 mmol) and SMA (0.2500 g, 0.125 mmol) in 4 mL of THF was stirred at room temperature for 2 h. After 2 h, the Et_3N was slowly dripped into the mixture. Then, the polymer solution was diluted to 2 mg/mL of DMF and drop-coated onto the 3 cm $\times$ 2.5 cm ITO-coated glassy substrate in the vacuum oven. After dropping on the ITO glass, most of the solvent was removed in the vacuum oven at 50 $^\circ\text{C}$. Then, the temperature was raised to 120 $^\circ\text{C}$ for 2 h and 160 $^\circ\text{C}$ for 10 h in a vacuum for the thermal imidization and forming of the resulting polyimide film.

Synthesis of Ionized-Cross-Linking Polymers. The synthesis of polymer iS3Ph is an example to illustrate the general synthetic route. The typical procedure was as follows: a mixture of 3Ph (0.1644 g, 0.125 mmol) and SMA (0.2500 g, 0.125 mmol) in 4 mL of THF was stirred at room temperature for 2 h. Then, the polymer solution was diluted to 2 mg/mL of DMF and drop-coated onto the 3 cm $\times$ 2.5 cm ITO-coated glassy substrate in the vacuum oven to remove most of the solvent to obtain the resulting polymer film. Afterward, the film was immersed in Et_3N for 15 min for ionization and then dipped in acetonitrile for 5 min three times to remove excess Et_3N .

Results & Discussion

To explore the interchain distance of cross-linking polymers, wide-angle X-ray diffraction (WXRd) measurement was applied, as depicted in **Figure 2a**. All polymers exhibited a broad diffraction peak at approximately 18° , indicating the presence of ordered domains within the amorphous polymer matrix. The calculated d-spacing values from the WXRd of the polymers, were 4.47, 4.79, 5.12, and 5.33 Å for **L3Ph**, **S3Ph**, **S5Ph**, and **S7Ph**, respectively. These values corresponded to the interchain distance between the polymer chains in the direction perpendicular to the triarylamine plane, demonstrating that expanding the triarylamine plane size could produce a more significant interchain distance.

To evaluate the diffusivity of the counterion upon the redox process, the diffusion coefficient (D) was determined by utilizing the Warburg coefficient (σ_w) within the low-frequency range in the EIS diagram. The experimental outcomes are depicted and presented in **Figure 2b**. According to the results, the D value of **S3Ph** exhibited one order larger than **L3Ph**, implying that the crosslinked structure significantly promoted the counter-anions (BF_4^-) migration within the polymer matrix. Among the crosslinking polymers (**S3Ph**, **S5Ph**, and **S7Ph**), BF_4^- possessed a higher migration capability through the polymer matrix along with enlarging the triarylamine plane, resulting in a significant promotion in diffusion. In addition to the increased interchain spacing, ionization could significantly enhance counterion diffusion. The ionized polymers, **iS3Ph** and **iS5Ph**, showed a considerable improvement in diffusion coefficient (D) around 192 and 4 times greater than the corresponding imide-type films, respectively, indicating that the triethylammonium/carboxylate complexes could accelerate the counterion migration. As a result, synergistic effects of interchain distance enlargement and ionization could be obtained, such that the D value of **iS5Ph** was 2,418 times greater than **L3Ph**.

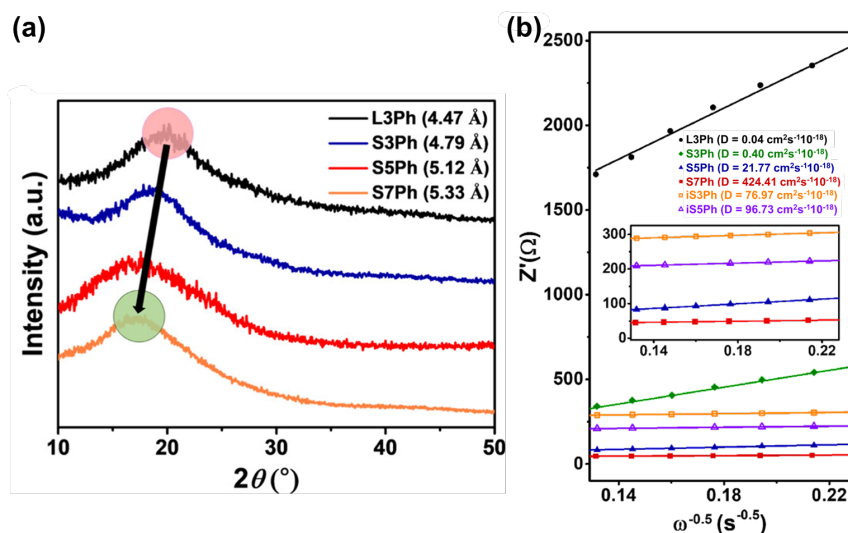


Figure 2. (a) WXRd patterns of imide-type polymer films (thickness: $95 \pm 7 \text{ }\mu\text{m}$). (b) the fitted linear plot between Z' and $\omega^{-0.5}$ in the low-frequency region and diffusion coefficient D of corresponding polymers.

The crucial properties of switching response capability and redox stability for the resulted ECDs in this study were investigated by using a square wave potential step method between 1.3 V for **L3Ph/HV**, 1.1 V for **S3Ph/HV**, and **iS3Ph/HV**, 1.0 V for **S5Ph/HV**, **S7Ph/HV**, and **iS5Ph/HV** as coloring voltage and -0.3 V as bleaching voltage. According to the results from **Figure 3**, the ECDs with increasingly more considerate interchain distances demonstrate a shorter response time in t_c or t_b than those with smaller interchain spaces. Besides enlarging the interchain distance, the ionization approach could be even more influential in enhancing ECD behaviors. After ionization, **iS3Ph/HV** and **iS5Ph/HV** showed a considerable improvement in response time, taking only 2.5 and 1.7 s in the coloring process, respectively.

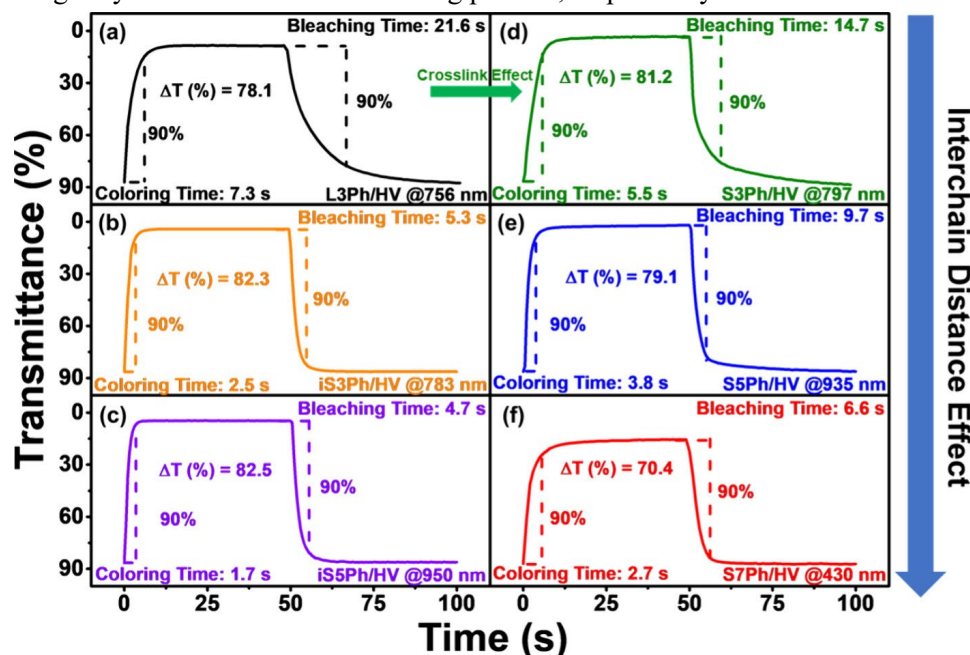


Figure 7. Switching response time of (a) **L3Ph/HV**, (b) **iS3Ph/HV**, (c) **iS5Ph/HV**, (d) **S3Ph/HV**, (e) **S5Ph/HV**, and (f) **S7Ph/HV** of ECDs with $2\text{ cm} \times 2\text{ cm}$ active area containing 0.03 M of HV and 0.1 M of TBABF₄ as the supporting electrolyte in 0.05 mL PC with 10 wt% of PMMA (polymer film 210 ± 15 nm in thickness).

Conclusion

This study systematically investigates a series of triarylamine-based polymers to examine the impact of expanding the interchain distance and ion exchange modification on the EC polymers. Among all series, **ieS5Ph/HV** showed a synergistic effect, leading to excellent performances of corresponding ECD. These findings highlight the significant impact of utilizing **SMA** as an optoelectronic material and the facile approaches by enlarging the interchain distance and implementing ion exchange modification on the electrochromic performance of the polymers.

Reference

- [1] Li, H. L.; Shao, Y. J.; Chang, C. W.; Liou, G. S. Styrene-maleic anhydride copolymers for high-performance triarylamine-containing electrochromic materials. *ACS Appl. Polym. Mater.* **2024**, *6* (6), 3554–3563.