A facile approach for preparation of triphenylamine-containing electrochromic polyvinyl acetals

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Abstract

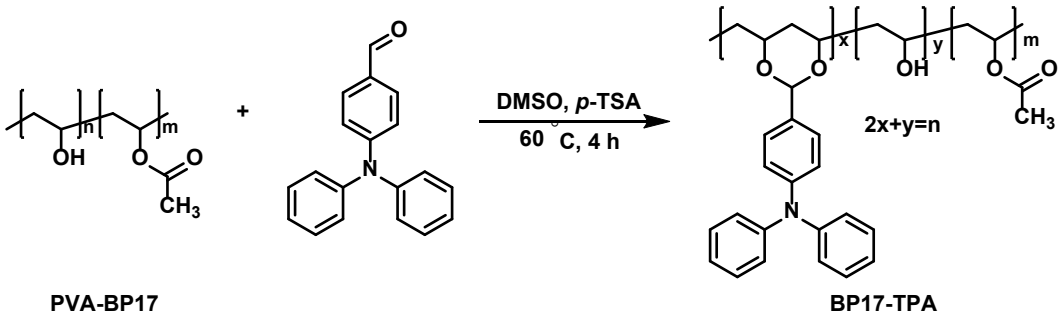
Polyvinyl acetals have remarkable adhesive, high optical clarity, and high water resistance and thus are widely used in various applications, such as safety glasses, primers, coatings, etc. In this work, the aldehyde-containing triphenylamine (TPA) was used to modify polyvinyl alcohol (PVA) by forming acetal units in the side chain. In this facile way, the prepared polymer shows unique dual emission behavior either in the solution or film states. Besides, after undergoing an electrochemical coupling reaction, the resulting polymer (BP17-c-TPA) still exhibits high transparency and colorless behavior in the neutral form, which is beneficial for electrochromic application. Its response capability displays a remarkably short-switching time for bleaching. This approach is cost-effective compared to conventional triarylamine-based anodic electrochromic polymeric materials and reduces many synthetic procedures for preparing electrochromic materials. Furthermore, the gel-type electrochromic devices (ECD), ECD-BP17-c-TPA, was fabricating and revealed prompt switching behavior that t_c and t_b are 1.71 s and 1.96 s, respectively, with the coloration efficiency of about 360.5 cm^2/C.

Introduction

Electrochromism (EC) is an attractive optoelectronic material because it is an absorption mode display and shows low light stimuli to our naked eyes. Thus, plenty of researchers focus on the development of versatile materials to apply in the electrochromism, such as small organics (viologens), inorganics (WO_3), metal complexes (Prussian blue), and conjugated polymers (polyaniline and polythiophene). [1] Among the published EC materials, triphenylamine (TPA) derivatives perform superior optical properties, such as a colorless and transparent appearance in the neutral state, easy-to-functionalized, multi-color change capability, and electrochemically reversible redox process. [2-3] However, conventional TPA-based electrochromic polymeric materials have complicated synthetic routes to prepare the electroactive monomers following the polymerization. Sometimes, the synthesis is accomplished with a high-temperature reaction, expensive starting chemicals, and catalysts, limiting the TPA electrochromic polymers to commercialization. Therefore, in this work, we aim to use poly(vinyl alcohol) (PVA) to functionalize with mono-aldehyde-containing TPA monomer to prepare the corresponding poly(vinyl acetal) (BP17-TPA). After the electrochemical coupling reaction, BP17-c-TPA, a crosslinking structure, revealed high response capability in the bleaching process.

Experimental

Preparation of TPA-containing poly(vinyl acetal)



In the 50-mL two-neck flask equipped with a magnetic stir, 0.400 g of poly(vinyl alcohol) (PVA-BP17) was dissolved in 6 mL DMSO at 100 ℃ for 12 hours. After the temperature was decreased to 60 ℃, 1.312 g of 4-formyltriphenylamine and 1.037 g of *p*-toluenesulfonic acid monohydrate were added to the solution and then reacted for 4 hours. After the reaction, the solution was precipitated in water, and the fiber-like crude product was obtained. The crude product was purified using Soxhlet extraction using MeOH and water for one day each. Then, the prepared poly(vinyl acetal) was dried at 75 ℃ for one day.

Results & Discussion

^{1}H NMR characterization

The following equation could calculate the acetalization of the prepared BP17-TPA:

$$Acetalization\ (\%) = \frac{Area(Acetal-H)\times 4}{Area(1.1\ ppm\ -2.0\ ppm)\times 0.82\times 0.85}\times 100\%$$

Where 0.82 is the content ratio of CH_2 in the poly(vinyl alcohol) main chain, and 0.85 is the hydrolysis degree. Therefore, according to **Figure 1**, BP17-TPA revealed the acetalization of 63.3% after calculation.

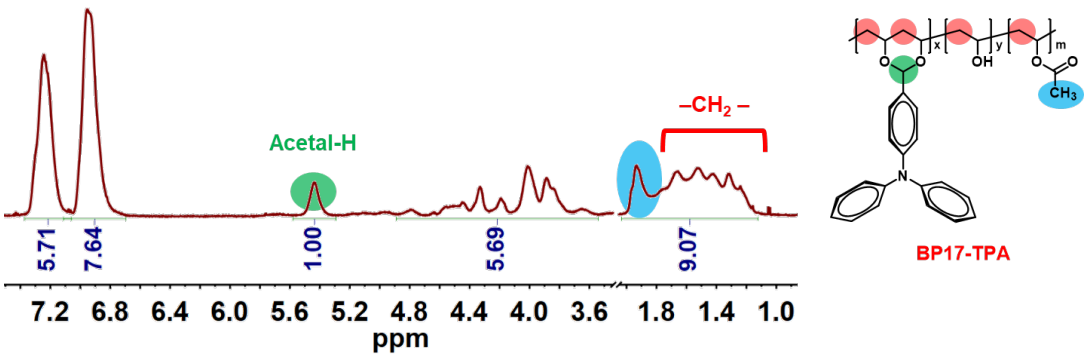


Figure 1. ^{1}H-NMR of BP17-TPA in DMSO-d_6.

Electrochemical coupling reaction and electrochemical properties

The BP17-TPA thin film was prepared using 2 mg of BP17-TPA in 1 mL DMAc and then drop-casting 400 μL of the solution on the 7.5 cm^2 ITO-coated glass substrate, following the 60 ℃/12 hours, 120 ℃/2 hours, and 160 ℃/4 hours thermal treatment in the vacuum oven. The thickness of the prepared film was around 400 ± 40μm. As depicted in **Figure 2**, BP17-TPA performed a high oxidation potential of over 1.0 V in the CV or DPV diagrams at the first scanning, while, at the second scanning, it generated a lower oxidation potential at 0.88 V, observed in the CV diagram (**Figure 2a**). This phenomenon could be attributed to the occurrence of the electrochemical coupling reaction at the *para* position of the TPA moieties to form the benzidine units. After 20-cycle CV scanning, the shape of the CV profile was maintained; thus, the coupling reaction was considered to end, and the prepared crosslinking film was called BP17-c-TPA.

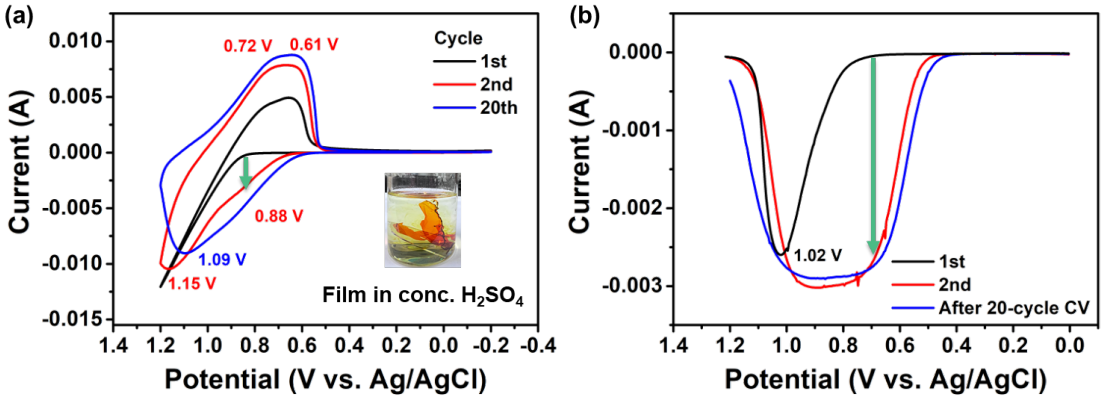
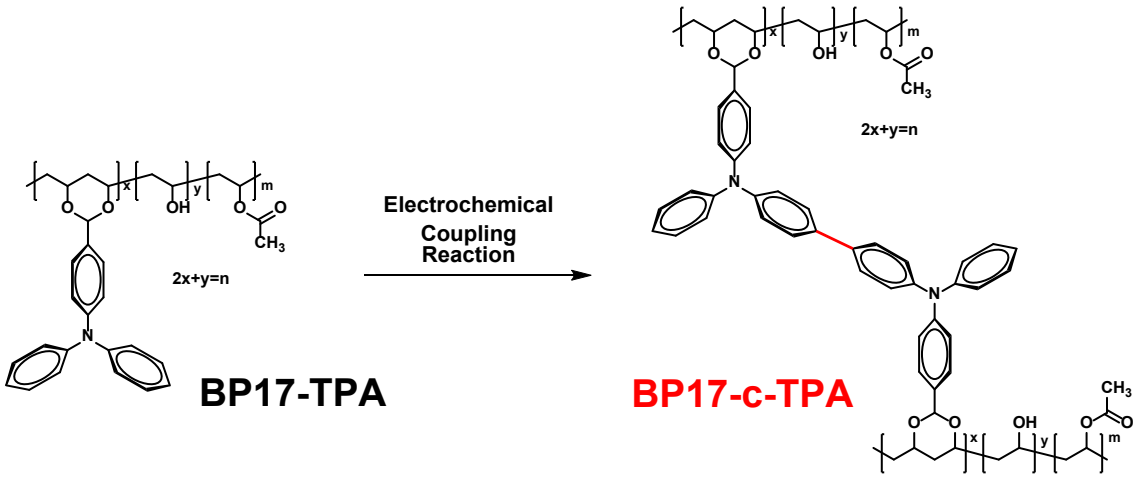


Figure 2. (a) CV diagram at a scan rate of 50 mV/s and (b) DPV diagram at an increment of 4 mV, pulse width of 25 ms, pulse period of 0.2 s, and pulse amplitude of 50 mV of BP17-TPA in 0.1 M $TBABF_4$/MeCN. (Thickness: 400 ± 40μm) (The insert photograph is BP17-c-TPA immersed in the concentrated sulfuric acid.)



Scheme 1. Schematic presentation of the electrochemical coupling reaction of BP17-TPA.

Electrochromic properties of the BP17-c-TPA

BP17-c-TPA showed two stages of color change, the brown and blue appearance at the first and second oxidation, respectively. Besides, at the first oxidation potential, BP17-c-TPA generated new absorptions not only in the visible region but also in the NIR region at 1350 nm due to the intervalance charge transfer (IVCT) in the benzidine units.

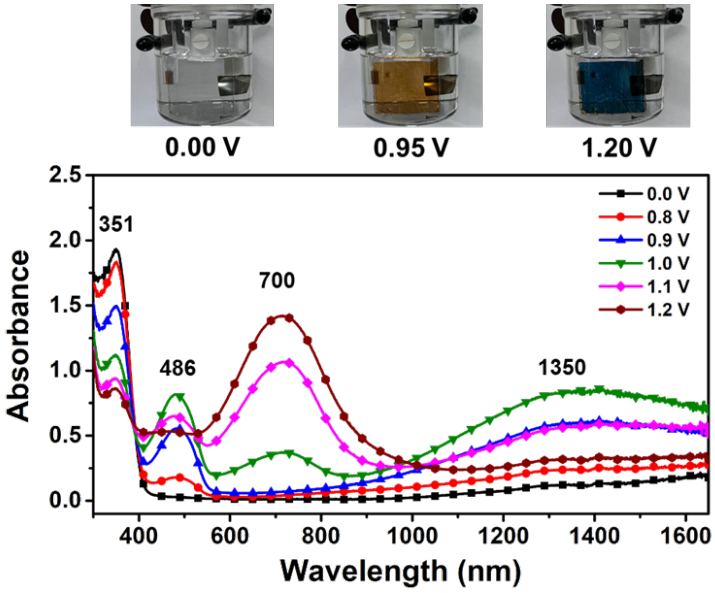


Figure 3. Spectroelectrochemistry of BP17-c-TPA investigated from 300 nm to 1700 nm in 0.1 M $TBABF_4$/MeCN. (Thickness: 400 ± 40μm)

Conclusion

In this work, we successfully prepared a low-cost TPA-based electrochromic material (BP17-TPA) using poly(vinyl alcohol) as the starting material. The synthetic route of BP17-TPA is a more facile and low-temperature preparation process compared to the conventional TPA-based EC material. The acetalization of BP17-TPA was well-characterized by the ^{1}H-NMR spectrum and showed 63.3% of the acetalization. After the electrochemical coupling reaction, the crosslinking polymer, BP17-c-TPA, revealed two-stage color changes from colorless to brown and then to blue. The results showed that PVA could be a potential candidate to apply for the optoelectronic applications.

Reference

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