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Electric field induced *cis*-to-*trans* isomerization of polyphenylacetylene in solid state

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A field induced isomerization from *cis* to *trans* form in stereoregular *cis*-rich polyphenylacetylenes (PPAs) was found, and it provides an alternate method to control the order of chromophores in thin solid films.

Polyphenylacetylene and its derivatives are conjugated polymers widely used in the field of ferromagnetic materials,[1] nonlinear optics[2] and electroluminescent diodes.[3] Recent research results have indicated that the optic/electronic properties of PPAs are directly influenced by the ordered structure. One strategy to control structural order is achieved by governing the polymerization process to obtain stereoregular conjugated polymers. Tang and his coworkers developed aqueous polymerization systems for the synthesis of stereoregular PPAs by organorhodium complexes.[4] The group also reported their investigations on the relationship between molecular structure and photoconductivity in substituted polyacetylenes as well as their doped composites.[5] Another is achieved by external propelling force. Thermal isomerization from *cis*-to-*trans* form in polymer chains of PPAs is a common phenomenon and has been well-studied.[6,7] Pressure-induced *cis*-to-*trans* isomerization of PPA's derivatives was also reported.[8] Considering the fact that PPAs are usually used in solid state and sandwiched devices working under applied electric field, it is of great interest to study the isomerization behaviour of PPA's thin solid films under electric field.

The stereoregular *cis*-rich PPA samples were synthesized and purified according to literature,[4] the *cis* concentrations ranged from 66.8 to 96.8%. All these samples are soluble in chloroform to form homogeneous solutions, which can be successfully cast into thin films. We cast PPA thin films on quartz plates for the UV-visible absorption measurement, and cast PPA films (*ca.* 20 μm) on a previously treated surface of aluminium substrates to fabricate single-layer photoreceptors, in which a stoichiometric amount of carrier transport material (*N,N*′-diethylaminobenzaldehyde-1-phenyl-1′-α-naphthylhydrazone) was introduced during the preparation of PPA solutions. The photoconductivity of obtained single-layer photoreceptors was measured with standard photo-induced discharge xerographic experiment, the details of the experiment were described elsewhere.[9]

After negatively charged to an initial surface potential V_i, the photoreceptors were illuminated at a light of 570 nm and 60 lux. The photogenerated holes migrated toward the charged surface by the aid of external field, and neutralized the surface charges; as a result, the surface potential decreased. The photosensitivity (S) was defined as the product of the light intensity and the discharge time from V_i to its half value under exposure to light ($t_{1/2}$). The relation between S and *cis*-concentration of PPA thin films is shown in Fig. 1. The S values decrease with increasing *cis*-concentration ranging from 66.8 to 96.8%. Similar experimental results were previously reported by ourselves[5] and Kang *et al.*,[10] the photoconductivity of PPA and its derivatives was mainly associated with the *trans*-segments on polymer chains.

Fig. 2 demonstrates the evolution of the photosensitivity of PPA thin films as a function of charging time, a higher photosensitivity is associated with a longer charging time. Note that increasing the charging time has resulted in little change in the electric field across the PPA films. For example, when the time for charging on a PPA film of 66.8% *cis*-concentration changed from 1 to 10 s, the variation of field strength was only from 5.39 to 5.50 × 10^5 V m^{-1}; and variation of the fields from 4.00 to 3.95 × 10^5 V m^{-1} was recorded with respect to the PPA film of 96.8% *cis*-concentration. So little change in the electric field cannot lead to an evident enhancement of the electron–hole pair dissociation and carrier transport efficiency.[11] In comparison with the results given in Fig. 1, a reasonable explanation to the increase of S could be the decrease of *cis*-concentration, in other words, there might have occurred a process of electric field induced isomerization.

To verify the deduction above, we examined the changes in *cis*-concentration before and after corona charging by UV-visible spectra. Based on the results reported by Ishii *et al.*,[12] the absorption spectrum of *cis*-transoidal(*cis*) segments in PPA polymer chains will show the feature of a plateau peak with a shoulder at around 390 nm, which is attributed to the π–π* transition of the main chain, and a peak at about 260 nm, which

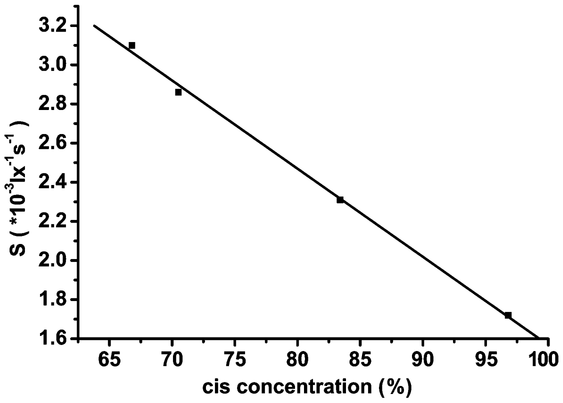

Fig. 1 Relationship between *cis* concentration and photosensitivity (S) of PPA. The single layered photoreceptors were illuminated by a light of 573 nm and 60 lux.

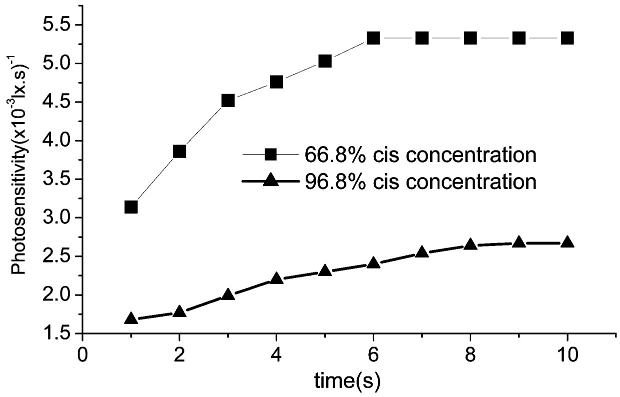

Fig. 2 Time course of photosensitivity change of PPA photoreceptors caused by corona charging.

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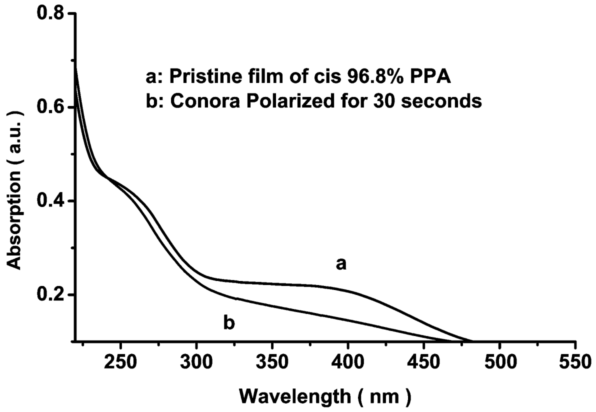
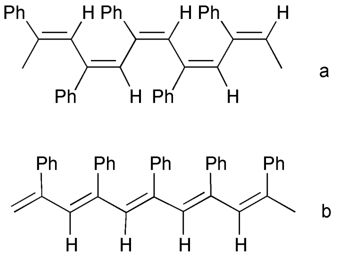


Fig. 3 UV-visible absorption spectra of *cis* 96.8% PPA and its corona-charging isomer. The thin film of *cis* 96.8% PPA was charged by corona for 30 s in the dark.

is due to the side chain. The absorption bands of the main chain and side chain for *trans*-transoidal(*trans*) segments shift to about 250 and 220 nm respectively.[12] The absorption spectra of the thin film of 96.8% *cis*-concentration PPA before and after corona charging for 30 s are shown in Fig. 3. The absorption plateau peak at around 390 nm becomes increasingly weak. This indicates the decrease of the concentration of *cis*-segments on PPA molecular chains.



a: cis-transoidal (cis), b: trans-transoidal (trans)

Scheme 1 (a) *cis*-Transoidal(*cis*) and (b) *trans*-transoidal(*trans*) configuration of PPA.

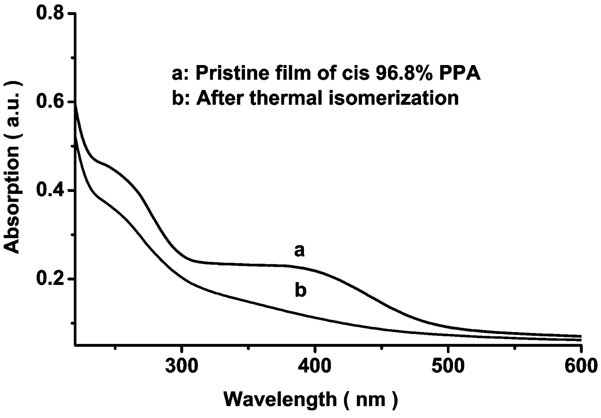


Fig. 4 UV-visible absorption spectra of *cis* 96.8% PPA and its thermal isomerization product. The thin film of *cis* 96.8% PPA was heated at 130 °C for 15 h.

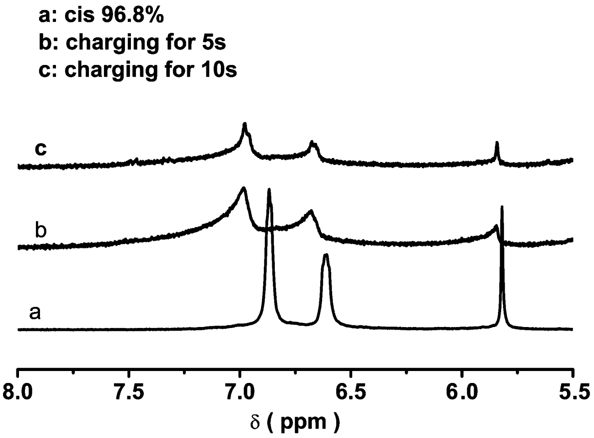


Fig. 5 ^{1}H-NMR spectra of PPA solution with an initial *cis* concentration of 96.8% (a) before and (b, c) after corona charging; solvent (a) THF-d_8, (b, c) CD_2Cl_2.

By heating to about 130 °C at inner atmosphere, the *cis*-transoidal segments in *cis*-rich PPA can be thermally transformed into *trans*-transoidal (See Scheme 1).[6,7] With the same PPA sample of 96.8% *cis*-concentration, a comparative study was conducted by absorption spectra recorded before and after thermal isomerization. The change in the spectral feature (Fig. 4) is almost identical to that in Fig. 3. It strongly confirms that there is an electric field induced isomerization. The stereostructure of PPAs can also be elucidated by ^{1}H-NMR spectroscopy analysis. In a standard ^{1}H-NMR spectrum of PPA with both *cis*-transoidal and *trans*-transoidal segments on polymer chains, the peak at 5.84 ppm is due to the absorption of a *cis*-proton, while the peak at 6.78 ppm to a *trans*-proton.[4] Fig. 5 demonstrates the ^{1}H-NMR spectra measured from the pristine PPA sample (96.8% *cis*-concentration) and the samples charging for 5 and 10 s. The *cis*-concentration in the PPA films, which were calculated from the obtained ^{1}H-NMR spectra,[13] changed from 96.8% to 92.6% and 71.8% respectively. The ^{1}H-NMR experiment results give quantitative support and lay a solid background to our explanation that the improvement of photoconductivity results from the field induced isomerization.

In conclusion, we have found an electric field induced isomerization process in PPA thin solid films. This is a new technique to control the structure order of *cis*-rich PPA. In comparison with the established methods such as thermal isomerization and pressure induced isomerization, electric field induced isomerization is more significant not only from the scientific point of view but also for practical application in optic/electronic devices.

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