

Polymer Communication

# Reversible ionochromism of self-layered polydiacetylene functionalized with hydrazide bind

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The topochemical process by which some diacetylenes (DAs) develop blue, red, green or other colors is a type of solid-state polymerization induced by ultraviolet or high-energy irradiation or by heating. Since its discovery, numerous approaches on the topochemical polymerization of DAs have been proposed and developed to date [1,2]. Recently we have observed the ability to construct very stable dispersions of supramolecular polymers from the doubly hydrogen bonded complex of terephthalic acids containing pendant DA groups. The phase separation of apolar DA side groups stabilized the terephthalic acid core through self-assembled layers of molecules. These terephthalic acid systems underwent a remarkable reversible color change upon thermo-stimuli [4].

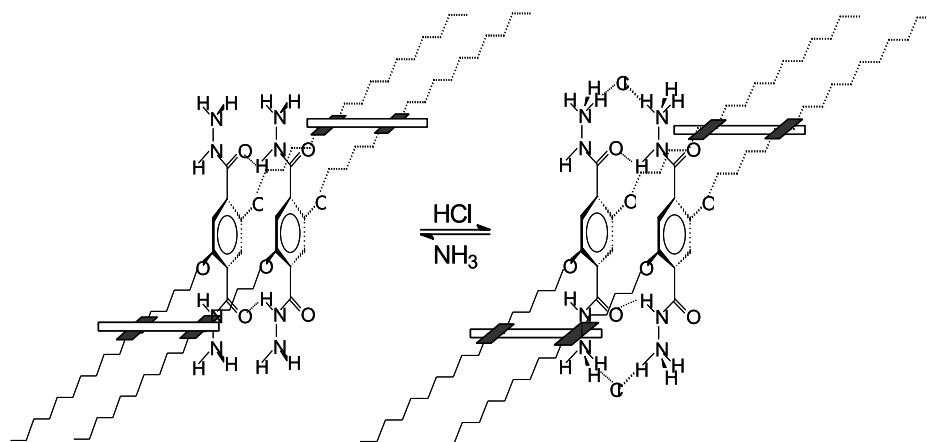
In this communication, we report another novel class of similar supramolecular polymers containing diacetylene (DA) moieties in the side groups with hydrazide bind. Compared with other approaches that have been demonstrated to be effective to create polydiacetylenes (PDAs), this method has a unique feature in that the PDAs can be obtained easily on spin-coated films and exhibit ionoreversible color switching. This allows the patterned two-dimensional structure ideal for sensor applications. Jonas et al. [3] described hydrazide derivatives of single chain DA lipids showing an unusual color change in polymerized vesicles depending on the pH of the surrounding medium. Similarly, we used hydrazide head groups instead of acid heads that provide four hydrogen-bonding sites and could also be altered by protonation of the terminal nitrogen. The synthesis of the hydrazide derivatives could be achieved by converting the oxyalkyl substituted terephthalic acids with carboodiimide as a condensing agent into the corresponding

hydroxysuccinimide diesters and then transformed into the hydrazides (white solid) by treating with hydrazine hydrate. In samples designated DA-(4,10) hydrazide, (4, 10) refers to the number of methylene units in the spacer between the aromatic and DA unit and tail region of the side group from DA unit, respectively. The chemical structures of these DA monomers are drawn in Scheme 1. X-ray diffraction pattern for the monomer and polymer showed that it is assembled into ordered layers similar to the comb-shaped rod-like polymers [5] (Fig. 1). Subsequent solid-state photopolymerization of the sample was done by UV irradiation under different acid–base conditions. The monomer solution dissolved in dichloromethane (2.5 wt%) was filtered through a 0.2  $\mu\text{m}$  membrane filter and spin-coated using a Headway Research spin coator (2000 rpm, 2 min). Spin-coated films of about 0.5  $\mu\text{m}$  on quartz plates were used here as they can be successfully photo-polymerized via a topochemical reaction and thereby easily produce the colored PDAs upon irradiation with UV of 254 nm wavelength. However, we found that the monomer conversion was much better for the films exposed to concentrated HCl. The X-ray data (Fig. 1(d)) indicates that this increase in conversion may arise from an improved ordering of the sample by the particular complexation interactions in the presence of HCl (Scheme 1).

Fig. 2 shows the absorption spectrum changes of the films untreated and pre-treated with HCl before and after UV exposure. The results indicate that only the red ( $\lambda_{\text{max}} = 550 \text{ nm}$ ) form of the polymer appeared for the untreated sample upon UV exposure; by contrast both of the red ( $\lambda_{\text{max}} = 575 \text{ nm}$ ) and blue form ( $\lambda_{\text{max}} = 635 \text{ nm}$ ) appeared upon irradiation for the film exposed to HCl vapor. Furthermore, the characteristic absorption band with  $\lambda_{\text{max}} = 335 \text{ nm}$  was red-shifted by 23 nm when exposed to HCl. Note that a fractional monomer conversion after photo-polymerization for these spin-coated films ( $\sim 15\%$ ) determined by isolating the insoluble part was also much

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Scheme 1. The chemical structure of PDA-(4,10) hydrazide dimer in the presence of HCl and  $\text{NH}_3$ . Two oxyalkyl side groups containing PDA units (rectangular bars) are perpendicularly attached to illustrate the whole molecular architecture.

lower than for the dispersion specimen (79%) in Ref. [4]. This spectral shift and the formation of the blue form PDA indicate that HCl exposure leads to a better stacking of the aromatic cores, resulting in a more effective DA packing for the topochemical polymerization to occur [6,7].

To investigate the reversible iono-chromic transition of the sample, we have measured UV-vis and FT-IR absorption spectra for PDA films before and after repeated treatments with  $\text{NH}_3$  followed by HCl vapors. After exposure to 28%  $\text{NH}_3$  vapor the blue film was readily converted into red polymer with absorbance maximum at 540 nm (excitonic band) and 500 nm (vibronic band) and a red-shifted characteristic absorption band with  $\lambda_{\text{max}} = 358$  nm was returned back to its initial position before UV irradiation. Unlike the parent carboxylic acids, after exposure to HCl the films of the synthesized hydrazides were easily converted into the blue polymer upon UV irradiation and a reversible color change underwent when alternatively exposed to HCl and  $\text{NH}_3$  vapor. This chromic transition occurred very fast (2 s). In situ FT-IR analyses provided detailed information on the response of the spin-coated film to the  $\text{NH}_3$  and HCl vapors. As shown in Fig. 3, the sharp band at  $3302\text{ cm}^{-1}$ , which is assigned to the N-H stretch vibration of the primary amide, dramatically loses

intensity upon HCl exposure (3b) and a very broad band centered about  $2495\text{ cm}^{-1}$  appears, which is N-H stretch of the protonated amine salt ( $\text{NH}_4^+\text{Cl}^-$ ). Moreover, the carbonyl stretch peak changes from neutral form ( $1624\text{ cm}^{-1}$ ) to protonated salt form ( $1659\text{ cm}^{-1}$ ) accompanied by the reversible color change and  $\text{NH}_4\text{Cl}$  salt absorption at  $3147$ ,  $3051$ , and  $1410\text{ cm}^{-1}$  increase simultaneously. However, Fig. 3(c) indicates the spectrum is not affected by UV exposure even though the color of the film changes. With further treatments the film underwent an almost reversible colorimetric transition with successive salt deposition in the sample. X-ray diffraction data confirmed this: a new diffraction peak around  $2\theta = 32.65$  appears because of the  $\text{NH}_4\text{Cl}$  salt formation (Fig. 1(a)).

The reversibility of this absorption change suggests that the necessary structural integrity of the aromatic core in PDAs is not altered by acid-base treatments and the spectral changes between the blue and red forms might be attributed to their different stacking robustness of the core group. In fact, the addition of HCl produces rigid core networks through H-bonding interactions and such sterically controlled systems have less degree of freedom to respond to intra-layer strain that causes structural modifications of the side PDAs. Thus the iono-chromic transitions for this material are dominated by the flexibility of the aromatic core packing. To gain more insight into the microscopic origins of the observed iono-chromic response of PDAs, conformational analyses for the alkoxy-substituted monomers, the neutral hydrazide and its HCl salt, were performed using molecular mechanics with Cerius 2 version 4.0. The energy minimum conformations were calculated by the model with the universal force field (UFF) based on the layer geometry previously studied [8] and emphasis was placed on the core group structure with DA side chains being omitted. The possible calculated structures are illustrated, still not fully identified, in Scheme 1. The phenyl rings are stacked in parallel with each other to maximize their  $\pi$ - $\pi$  interactions. Furthermore, the amide

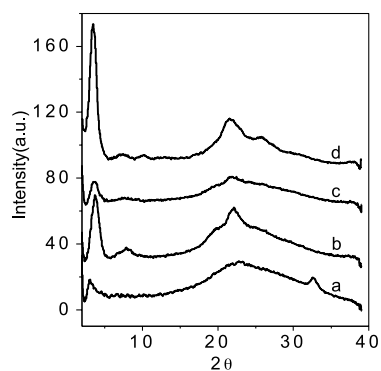


Fig. 1. XRD patterns of DA-(4,10) hydrazide and (a) PDA (b) DA powder (c) DA spincoated (d) DA HCl.

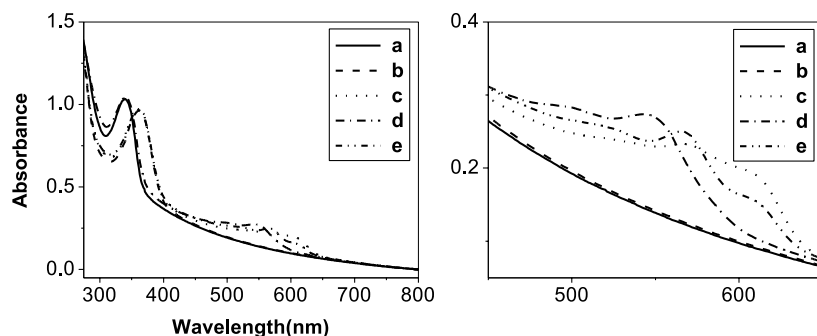


Fig. 2. Reversible colorimetric transitions of a spin-coated film on a quartz plate. (a) Monomeric film, (b) exposed to HCl (37%) vapor for 15 min, (c) UV exposed for 8 min, (d) exposed to  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (28%) for 1 min, (e) exposed to HCl vapor for 1 min.

groups and the terminal amine hydrogens and their free electron pairs in the salt form also form H-bonds by the HCl molecules inserted between two core groups. The chlorine anions are coordinated to the hydrogens of the positively charged ammonium moieties and thereby form a network structure by bridging the neighboring core groups. This insertion of the chlorine anion is consistent with the increase in the amine–nitrogen distance between two DA monomers from 0.40 nm (neutral) to 0.43 nm (salt) (Fig. 1(d)).

The reversible change between blue and red forms under acid–base treatments thus can be explained by the change in the structure of the core group affecting the packing of the side PDA chain. When HCl molecules are inserted among hydrogen bonded hydrazide head groups, the resultant H-bonding network structure leads to more ordered side chain conformation and maintains an extended chainlike shape,

resulting in an efficient  $\pi$ -electron conjugation, and the polymer absorbs in the red region to give a blue form. On the other hand, the  $\text{NH}_3$  vapor eliminates HCl molecules from the complex structure and the increase in motional freedom of the side PDA chains allows a more disordered and less coplanar polymer with a lower conjugation length thereby producing a red form [9].

The unusual iono-chromism along with easy processing described here, which is beneficial for PDA's envisaged application as a surface coating for biomedical and optoelectronic applications, should expand the scope where the PDAs can be realized and applied.

### Acknowledgements

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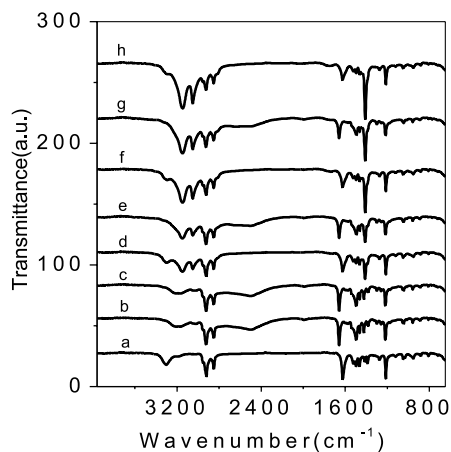


Fig. 3. FT-IR spectra of spin-coated film of sample on NaCl plate. Monomeric film (a), exposed to HCl vapor for 15 min (b), UV exposed for 8 min (c), exposed to  $\text{NH}_3 \cdot \text{H}_2\text{O}$  for 1 min (d), exposed to HCl vapor for 1 min (e), exposed to  $\text{NH}_3 \cdot \text{H}_2\text{O}$  for 1 min (f), exposed to HCl vapor for 1 min (g), and exposed to  $\text{NH}_3 \cdot \text{H}_2\text{O}$  for 1 min (h).