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Reversible Thermochromism in Hydrogen-Bonded Polymers Containing Polydiacetylenes**

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Numerous diacetylene (DA) derivatives have been synthesized and incorporated into polymerized assemblies for their potential applications as optoelectronic devices and biosen-

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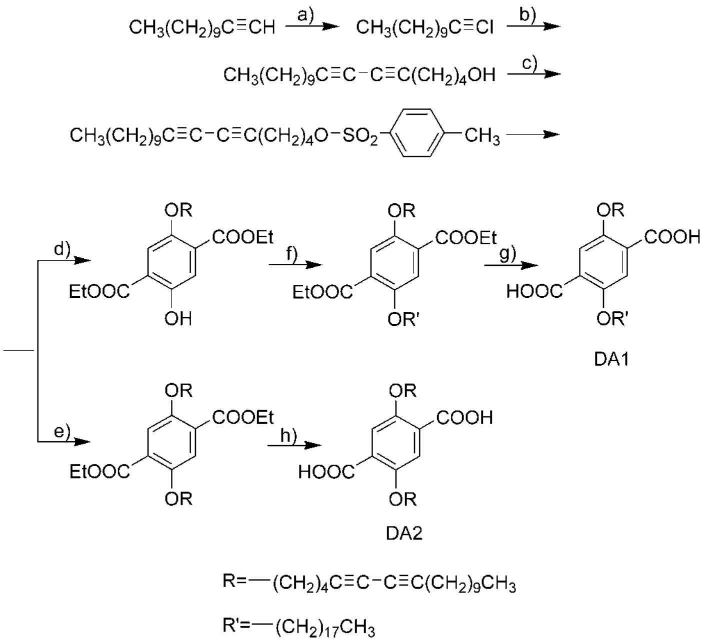
sors.[1] The most extensively studied systems are self-assembled or surface-attached layers (vesicles and Langmuir–Blodgett films) containing polydiacetylenes (PDAs).[2] Much less explored systems include large molecules containing dyes or other functional units bridged by a DA group.[3] With these materials substantial progress has been made in understanding the nature of the polymerization of DA moiety, the spectral changes, and the thermochromic transitions of PDAs. The rationale behind our work is that by choosing the appropriate substituents the supramolecular polymeric system will provide a specific order of the reactive groups and promote a certain degree of flexibility to accommodate structural changes during the polymerization and subsequent color changes of the PDA. In the construction of supramolecular polymers hydrogen bonding plays a prominent role because of its directionality and versatility. However, hydrogen bonds between aromatic dicarboxylic acids have rarely been used to form supramolecular polymers.[4] Recently we have been able to construct very stable dispersions of supramolecular polymers from the doubly hydrogen-bonded compounds of long dialkoxy substituted terephthalic acids.[5] The phase separation resulting from the presence of the apolar side-chain groups stabilizes the terephthalic acid core through the formation of self-assembled layers of molecules. Herein we report a novel class of similar supramolecular polymers containing DA moieties in the side chains. Using these hydrogen-bonded terephthalic acid DA compounds allows the easy preparation of PDAs with characteristics, such as thermoreversible color switching, which differ significantly from those of conventional systems.



Scheme 1. Preparation of the compounds DA1 and DA2. a) I_2, b) $HO(CH_2)_nC{\equiv}CH$, c) *p*-toluenesulfonyl chloride, d) and e) diethyl-2,5-dihydroxyterephthalate, f) $CH_3(CH_2)_{17}Br$, g) KOH, h) KOH.

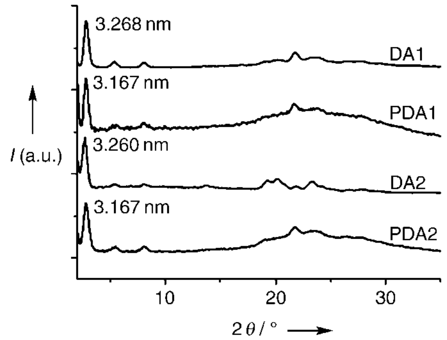


Figure 2. Powder X-ray diffractograms of DA1, PDA1, DA2, and PDA2 at 25 °C. Polymers prepared in dispersion (CHCl$_3$/hexane).

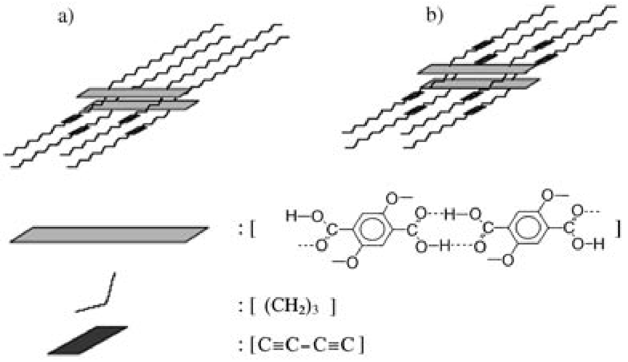


Figure 1. Stacking structures of the compounds a) DA1 and b) DA2.

The structures of our materials and their synthesis are schematically shown in Figure 1 and Scheme 1. The powder X-ray diffraction results were not sufficient to allow a complete indexing of all the reflections but confirmed that during the photopolymerization process the highly ordered layer structure is preserved with slightly decreased interlayer spacings and side-chain crystallinities (Figure 2). These DA compounds DA1 and DA2 (Scheme 1) are soluble in common organic solvents, can be deposited by casting or spin coating, and even before polymerization display some typical polymeric properties, such as high solution viscosities. To understand the influence of the DA content and its specific molecular packing within the side chains on the layer structure and thermochromism of the PDAs (PDA1 and PDA2), we examined the polymerization behavior for the two compounds DA1 and DA2 upon exposure to UV light. The polymerization of DA groups, which is a topochemical (or topotactic) polymerization, requires specific molecular position and orientation in the solid-state, which gives rise to a lot of barriers to their production. In our materials the DA groups could be polymerized either in a simple dispersion medium of chloroform/hexane or in spin-coated films. Figure 3 presents the comparison of the UV/Vis spectra for DA1 in various sample forms before and after UV exposure. The spectra for DA2 are omitted because the spectra of DA1 and DA2 are nearly identical except the relative intensity ratio I_{PDA}/I_{DA}. The not-polymerized sample in a CHCl$_3$

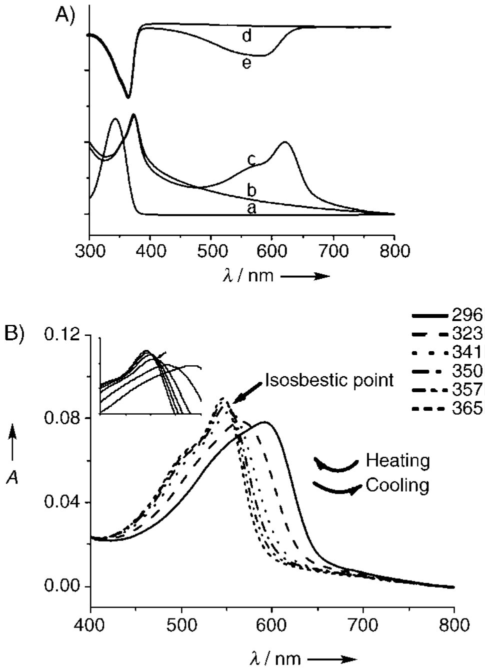


Figure 3. A) UV/Vis absorption (a,b,c) and transmission spectra (d,e) of: a) DA1 in $CHCl_3$ solution, b) a dispersion of DA1 in $CHCl_3$/hexane (0.5 % *v*/*v*) unexposed and c) exposed to UV irradiation (254 nm, 23 $mWcm^{-2}$) for 20 min, d) a spin-coated film of DA1 on quartz unexposed and e) exposed to UV irradiation for 1 min. B) Reversible colorimetric transitions of a spin-coated film made from PDA1 as thermal stimulus was imposed and removed at the indicated temperatures.

solution, in a dispersion of $CHCl_3$/hexane, and as a film show no absorption peaks in the region from 400 to 720 nm and all these probes fluoresce when irradiated with UV/Vis light. A characteristic absorption band of the dispersed phase with λ_{max} around 370 nm is red-shifted by 25 nm relative to the corresponding band in solution. A similar absorption band is also observed for the spin-coated film. This excitonic absorption shift can be understood as an indication that under the given experimental conditions supramolecular polymers form an aggregate by parallel stacking of the aromatic rings of the terephthalic acid cores and the side chains (Figure 1).[6] The assembly of the aromatic groups into a rigid core by stacking is a prerequisite for the formation of the layered architecture which is required for the DA units to react topochemically. As shown in Figure 3, the absorption spectrum for the dispersion sample has a distinct maximum at 640 nm with a shoulder around 580 nm after UV irradiation, which is characteristic for PDAs. When the irradiation time is extended to 20 min, the absorption intensity of the so-called blue form of the polymer at 640 nm increased and the maximum only shifted slightly towards shorter wavelengths. Continuing irradiation for an hour results in a weak blue-form absorption band, leaving the red form at 580 nm dominant. The transmission spectrum for the spin-coated PDA sample is similar but has a blue-shifted absorption at 600 nm and another at 540 nm ascribable to the red form, which indicates the formation of a mixture of red and blue forms. Note that a fractional monomer conversion after photopolymerization for spin-coated films (≈23 %) determined by isolating the polymeric insoluble part (from the soluble monomer part owing to incomplete polymerization) was also much lower than for the dispersion specimen (79 %). We think that the localized shear stresses and the accompanying changes in samples and molecular dimensions produced during the spinning process drives the films to a more disordered "red" film as a result of the perturbation of the π-conjugation system. It is also of note that the topochemical polymerization observed for DA1 provides evidence for the spontaneous association of like–like side chains, a macroscopic expression of molecular DA recognition. As this compound has asymmetric side chains attached to the terephthalic acid units it seems unlikely that DA chains that are just held in position geometrically will be able to overcome thermal fluctuations and pack in a stable enough way for the topochemical reaction to occur in the liquid state.

To investigate the thermochromic transition of the spin-coated films, we measured absorption spectra against temperature based on the results of differential scanning calorimetry (DSC) measurements (Figure 4). These materials exhibit structural and thermal behaviors similar to the side-chain polymers based on a rigid backbone (see Supporting Information).[7] Their general architecture can be described in terms of hydrogen-bonded aromatic rigid backbones separated by layers composed of relatively well packed side chains. The two endothermic transitions observed by DSC before melting of the whole sample indicate that the properties of the rigid-backbone layers are considerably different from the properties of the side-chain layers. The low-temperature transition is attributed to the onset of disordering processes in the side-chain region, while the layered structure and thus the ordered arrangement of the backbones is maintained, the higher transition temperature is associated with motion of the rigid-core. As illustrated in Figure 3B, polymer PDA1 shows completely reversible spectroscopic changes during the thermal cycles. The blue form which gives rise to the band at 600 nm progressively disappears and the red form appears as the temperature increases. The absorptions of the red form appear at 540 and 500 nm at 350 K and then grow in intensity up to the melting temperature of 408 K even though the film was not fully blue to begin with. Upon cooling to room temperature the blue form reappears in a completely reversible manner. This remarkable thermochromic behavior is not usually observed in PDAs. To our knowledge, only a few examples have been reported to date.[8]

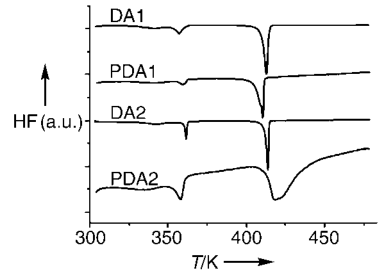


Figure 4. DSC traces of compounds DA1, PDA1, DA2, and PDA2.

A more detailed investigation of the spectra reveals that there appears to be an isosbestic point above the transition temperature of 352 K. It shows that increasing temperature merely increases the amount of the red form without passing through any observable new intermediate form. DSC data suggest that the spectral change above the transition temperature of 352 K is triggered by strain coming from the side-chain layers existing in a liquid state. Thermal stimulus gives the side chains enough energy to impose mechanical strain on the PDAs by rotation around the single bonds between the methylene units although such movement of the side chains must be restricted so that the necessary crystal integrity for reversibility is maintained. Theoretical calculations revealed that such a side-group motion could induce a change in the electronic structure of PDAs.[9] Thus, the origin of this chromism remains unclear but our data support a mechanism in which the red form, a form which indicates a diminished conjugation length, is merely a thermally equilibrated molecular fluctuation of the blue form. The observed reversibility in PDA2 (see Supporting Information) corroborates that the layer integrity is retained at higher annealing temperatures. In fact, polymerization of DA2 produces the unusual rigid ladder-type bonding in the layer structures (see Figure 1) and such sterically controlled systems have no degree of freedom to respond to intralayer strain that causes structural modifications. Thus up to the backbone melting temperature the thermochromic transitions for our material are dominated by the flexibility of the side-chain packing between supramolecular polymers.

The experimental data presented herein do not allow a conclusive molecular model to be constructed for the spatial arrangement of the PDA chains with respect to each other and the terephthalic acid plane. We can, however, conclude that the combination of double hydrogen-bonds between the hard terephthalic acid cores and a molecular recognition of DA moieties in the side chains, which enables topochemical polymerization to occur, allowed us to prepare PDAs in dispersed solutions or even in spin-coated films. The formation of stable, ultrathin polymer films is crucial for the envisaged application of PDAs as sensors for biological detection or coatings for optoelectronic applications. These materials also have thermochromic properties which allow a reversible color switching, thus expanding the scope of potential applications for polydiacetylenes.

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