High-Content Photochromic Polymers Based on Dithienylethenes

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Dithienylethenes (DTEs) are one of the most promising classes of photochromic compounds for use in optoelectronic devices such as waveguides, memory media and sensors. The development of DTE based polymers that contain a high mass-content of the photoactive DTE component, that maintain their photochromic activity in the solid-state and that are easily processed into thin-films under a variety of conditions is critical for the implementation of the materials into useful applications. This Microreview provides an overview of the current approaches for preparing DTE-based polymers and discusses some of the problems associated with the resulting materials such as poor solubility, low DTE content and poor photochromic activity. We present specific examples from our own research, which highlight our research group's contributions.

Introduction to Molecular Switching and Photochromism

Molecules that respond to the application of external stimuli by undergoing reversible transformations between two distinct structures have the potential to significantly influence the development of numerous important Materials Science and Structural Biology technologies.[1,2] This potential is based on the fact that, because the molecules typically undergo dramatic changes in their electronic and topological characteristics, they can act as switching elements and other dynamic components in various optoelectronic devices and functional materials.

Photons are particularly appealing stimuli because modern lasers can be used to achieve fast response times, to focus a fine-tuned stimulus on small localized domains without significant diffusion and to trigger photochemical

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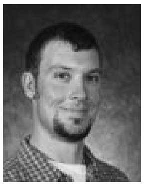

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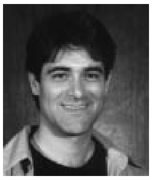

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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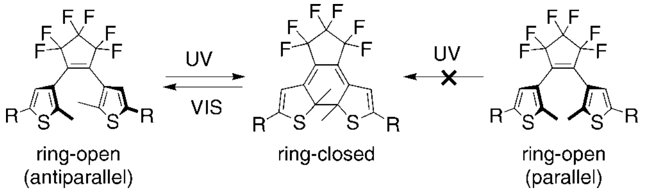
events under conditions mild enough to pose minimal danger to sensitive biomaterials. Compounds that interconvert between different isomers having unique absorption spectra when stimulated with light are referred to as photochromic and the process is called photochromism. In these systems, the changes in the electronic patterns responsible for the changes in colour also result in variations in other practical physical properties such as luminescence,[3–7] electronic conductance,[8,9] refractive index,[10–13] optical rotation,[14–16] and viscosity.[17,18] The photomodulation of these properties has the potential to significantly advance optoelectronic technologies such as waveguides,[19,20] read/write/erase optical information storage systems,[21] and actuators.[22,23]

Photochromic Dithienylethene (DTE) Polymers: Needs and Considerations

Among all the organic photochromic compounds, those possessing the hexatriene framework provided by the 1,2-dithienylethene (DTE) structure have attracted special attention. This attention is well earned because the DTEs satisfy the numerous physical and chemical properties required for practical use in functional materials technologies. DTE derivatives undergo reversible photocyclization reactions between their coloured ring-open and colourless ring-closed forms as illustrated in Scheme 1 with an impressive degree of fatigue resistance and thermal irreversibility.[1,2]



Scheme 1. Photoisomerization of the DTE backbone.

In addition to the favourable photochromic properties of DTEs, the electronic distribution of the conjugated system in the ring-closed form can be readily tailored by synthetically modifying the pendant groups located at the ends of the polyene system of the DTE backbone ("R" groups in see Scheme 1). This ability to fabricate designer materials adds to the appeal of DTE derivatives and makes them one of the most attractive classes of photochromic molecules for optoelectronic applications. However, in order to fully exploit these versatile compounds as photoresponsive functional materials, they must be converted into forms that can be readily processed, such as thin films. Despite this important need, the bulk of the reports on DTE systems have focused on evaluating the efficacy of photochromic systems either in solution or in a polymer matrix where they are introduced as dopents.

Dispersing the dye in a polymer matrix is by far the easiest strategy to prepare photochromic films, however, it has some serious limitations. Films with a high content of the photochromic unit are desirable but the preparation of such films using this strategy is a challenge due to segregation of the components upon long-term storage. Undoped photochromic polymers would be advantageous over their dispersed monomeric counterparts because a high concentration of the active photochromic component can be incorporated into a polymer film resulting in the amplification of the desired effect, while maintaining the optical homogeneity of the material.[24] For example Kim and coworkers[12] have shown that DTE polymer films have ten times less surface roughness than the equivalent films where the DTE is dispersed in polymethylmethacrylate (PMMA).

Three key issues that should be particularly noted when designing photochromic polymers relate to the choice of the matrix. The first two are general and are concerned with the compatibility of the polymerization process with functional groups on the monomers and the solubility of the resulting polymers. Special attention must be made to choose a polymerization procedure that is not adversely affected by the presence of the tunable "R" groups mentioned above. These are the groups that will be responsible for imparting the desired property into the material and their interference with the polymerization reaction are bound to have a detrimental effect. Polymers that show poor solubility in common solvents limit their use because it will be more difficult to cast them as thin films and may result in poor photochromic activity of the polymer relative to the monomers.

The third consideration relates to the microscopic flexibility of the matrix. The polymer matrix must be appropriately flexible to accommodate the conformational requirements of the photoisomerization reaction. This is particularly important in the case of organic photochromic compounds such as the DTEs. In this particular case, the ring-closing reaction can occur only from the *anti*-parallel conformation of the ring-open isomer (see Scheme 1). This conformational requirement was clearly illustrated by Irie and coworkers who showed that locking the DTE backbone in the parallel conformation prevents photochromism.[25] Within densely-packed polymer films, it is unlikely that the interconversion between parallel and antiparallel is feasible. Therefore, the polymer matrix must be disordered and flexible enough to allow for conformational interconversion. Alternatively, the matrix must, in some way, predispose the DTE into its productive antiparallel form.

Specific Examples Leading to High-Content DTE Polymers

This Microreview presents several current approaches for constructing functional DTE polymers. In it, we briefly describe some of the key examples that have contributed to the progress of the area. We also note, where possible, the synthetic methods to prepare each polymer as this may have a significant impact on what functionality can be used in each case.

Pendant DTE Polymers

Several copolymers containing the DTE backbone have been reported. Two examples developed by Tian[26,27] and

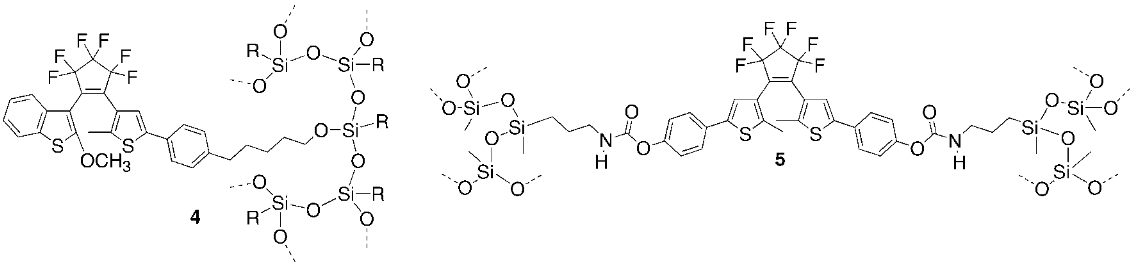

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Figure 3. Polysiloxane and silsesquinoxane materials containing DTEs.

Kim[12] are illustrated in Figure 1. An allylic DTE was copolymerized with methylmethacrylate (MMA) to produce copolymers of the type **1** containing less than 1% of the DTE component.[26] The quantum yields were notably high for both the ring-closing and ring-opening reactions in solution but were reduced to less than half these values when the polymers were processed as films. Copolymers of the type **2** were prepared by copolymerizing an allylic DTE with styrene and *n*-butylmethacrylate to produce copolymers containing as much as 22 wt.-% of the DTE component.[12] In these cases, the films showed good photoconversion (ca. 70%) and large changes in refractive index. This improvement in performance is most likely due to the presence of the bulky side-chain in methacrylate copolymers creating materials that can better accommodate the structural changes during the ring-closing reaction. However, the preparation of both materials relies on radical polymerization techniques, thus limiting the choices of pendant functionality on the photochromic backbone.

Ring Opening Metathesis Polymerization (ROMP) of strained bicyclic olefins using Grubbs's bis(tricyclohexylphosphane)benzylideneruthenium(IV) dichloride initiator has risen in popularity. This is due to its mild reaction conditions (it operates at or near room temperature even in water), its functional group compatibility (the process shows a high preference for strained C=C bonds and is indifferent to highly reactive functional groups such as alcohols, amides, aldehydes and carboxylic acids), and its ability to generate polymers with narrow molecular weight distributions. Also, the polymer chain length can be tailored by simply varying the catalyst to substrate stoichiometry. ROMP has the promise in industry of cleaner, cheaper and more efficient processes and appears ideal for our purposes.

The success and popularity of ROMP as a polymerization method led us to investigate its use in the generation of homopolymers from DTE derivatives[28,29] (Figure 2). Homopolymers provide the advantage over copolymers because they contain an even higher concentration of the photoactive component, although reduced photochromism may result from the higher densities. We originally prepared a family of DTE polymers, **3**, from appropriate strained bicyclic olefins attached onto the DTE backbone. The synthesis of each monomer is straightforward and consists of tethering the strained bicyclic olefin to the DTE through an ester linkage. The polymers can be prepared in good yields, they are soluble in a wide range of common organic solvents, they have narrow polydispersity indices (1.1–1.5) and they contain an impressive 63–69 wt.-% of the DTE component.

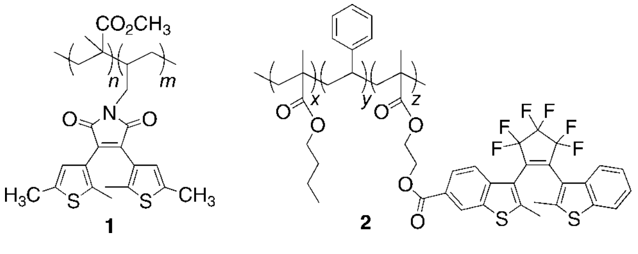
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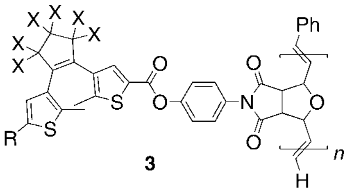
Figure 1. Copolymers containing pendant DTE units.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X = H or F, R = Cl or Ph, *n* = 25–100

Figure 2. Homopolymers containing pendant DTE units.

The polymers can be easily processed into thin films on quartz substrates using spin-coating techniques. A comparative UV/Vis study showed that the reversible photoisomerisation reactions of polymers **3** were efficient both in solution and in the solid state. It is important to note that similar photochromic conversions were achieved in the thin films as in solution, although slightly longer irradiation times were required in the former case. The low glass transition temperature (about –50 °C) of these polymers illustrate that there is enough microscopic flexibility provided in the material at room temperature to accommodate the conformational requirements of the ring-closing reaction.

Polysiloxane and silsesquinoxane polymers are particularly useful as polymer matrices for cyclization reactions because of their large free volume. The voids are appropriate residences for the DTEs. Recently, two approaches have been used to prepare such materials (Figure 3).

Irie and coworkers[30] prepared a silsesquinoxane based polymer **4** containing pendant DTE units. Materials containing less than 25 wt.-% of the DTE component were prepared by bonding allyl-functionalized DTEs to the polymer backbone using Pt-catalyzed hydrosilylation reactions. The large free volume in the polymer matrix allowed for good photoconversion to the ring-closed form (70–80%). Alternatively Boilot and coworkers[13] prepared highly cross-linked polysiloxane films (**5**) using sol-gel techniques (Figure 4). This approach can be used to prepare amorphous films by mixing all components, spin-coating and treating at 70 °C for 15 h. The materials had very high photochromic conversions (95%) and contained 40–50 wt.-% of the DTE component. In addition, the ring-closing reaction was accompanied by a large change in refractive index making them potentially useful in waveguiding applications.

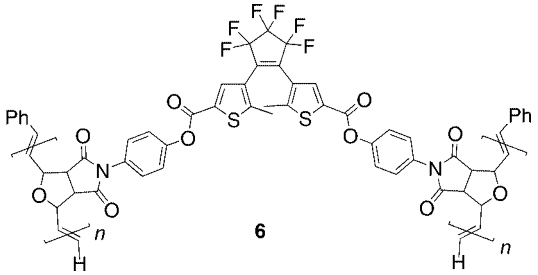

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Figure 4. A cross-linked DTE polymer.

The need for accommodating matrices is best illustrated by comparing our original homopolymers (**3**) to the cross-linked analogue **6**.[28] Cross-linking in the sol-gel film (see example **5**) did not appear to inhibit photochromism due to the large free volume in the films and the flexible side-chains linking the DTE skeleton to the polymer network. However, we found that the highly cross-linked polymer **6** prepared using ROMP exhibited low photoconversion to the ring-closed form when subjected to UV light. This limited photochromism is most likely a direct result of the conformational restrictions of the matrix and its inability to allow the DTE to convert to its active antiparallel form. Unlike the original ROMP materials (**3**), which require only a few atoms to move when the thiophene rings are rotating, the entire polymer chain must undergo significant movements in cross-linked polymer **6**.

A similar result was observed by Uchida and coworkers[31] who prepared high-content polymeric films by oxidative polymerization of phenol-functionalized DTEs **7** (Figure 5). The resulting highly cross-linked films were insoluble and amorphous in the case of the *ortho*-isomers. In the case of the *meta*- and *para*-isomers, no films were produced unless 10 wt.-% of 4,4-dihydroxyphenyl ether was added as a co-monomer. In all cases, the colouration was unremarkable and conversion to the ring-closed form was less than 20%. The authors make the reasonable claim that, like our cross-linked case, the polymer matrix has locked a significant amount of the DTE into its non-productive parallel conformation. This problem was circumvented by subjecting the monomers to UV light to produce the ring-closed form prior to the polymerization reaction. Polymerization of the ring-closed isomers produces a film where the pattern is predisposed to favour the productive antiparallel conformation and allow the photoisomerization reactions. Bis(benzothienyl) versions of the ring-closed forms were also prepared and polymerized under similar conditions. This resulted in polymer films, which nearly doubled in their photochromic conversion. These systems were used for non-destructive data storage using the changes in the IR spectrum as the readout signal.

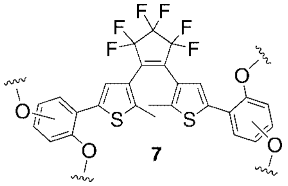

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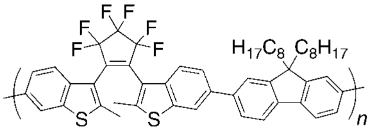
Figure 5. Phenol-functionalized DTEs.

Main-Chain DTE Polymers

Recently, several main-chain DTE polymers and copolymers have exhibited high cyclization quantum yields due to enforcement of the antiparallel conformation[9,32] (Figure 6).



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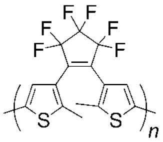

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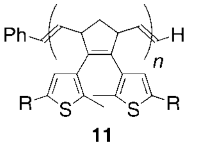
Figure 6. Main-chain DTE polymers exhibiting with high cyclization quantum yields.

Copolymer **8** was prepared by copolymerizing a bis(benzothienyl) DTE with fluorene to generate materials which exhibit photomodulation of conductivity.[9] The photoconversions in solution were low (35–40%) and decreased dramatically (11–14%) when the material was spin-coated as a thin film. These low conversions are not surprising considering recent studies on DTE dimers and trimers suggest that only alternate DTE units photocyclize.[33] The copolymers exhibited photomodulation of fluorescence where the closed form quenches the fluorescence of the open. Preliminary electrical conductivity experiments report a doubling of conductivity when the ring-open form is photoisomerized to the closed form. This behaviour is attributed to the increased π-conjugation in the ring-closed DTE polyene main chain.

A similar approach to constructing a DTE based main-chain copolymer **10**, which shows good photoregulation of fluorescence, was recently constructed by Kim and coworkers.[34] The copolymer was synthesized by a Wittig polycondensation method and consists of five alternating pairs of polyphenylenevinylene (PPV) and DTE units (Figure 7). This polymer architecture also seems to favour the antiparallel conformation. Upon photoisomerization of the DTE unit, the fluorescence of the polymer is regulated; the open form allows fluorescence of the PPV whereas the closed-form acts as a fluorescence quencher. However, because the excitation wavelength used to generate the fluorescence is in the UV region of the spectrum, where both forms of the DTE absorb, this system is destructive: the wavelength used to read the information also causes photoisomerization. It is critical to the success of photochromic optical data storage systems that the wavelength used to excite the fluorophore lies outside the absorption region of both forms of the photochrome.[21]



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R = Cl, CO_2Me, CO_2^-

Figure 8. Main-chain DTE homopolymers.

These examples clearly indicate that linking the DTE units directly or to aromatic spacers provides a material that prefers the antiparallel conformation. However these polymers and copolymers do not exhibit high photoconversions, as in the pendant DTE polymers. In addition these systems are not synthetically versatile and electronic variants cannot easily be synthesized using these methods because the “R” groups (see Scheme 1) have been sacrificed. In a recent article we have prepared a family of main-chain DTE polymers **11** by incorporating the cyclopentene directly into the polymer backbone using ROMP technology.[35]

Our approach takes advantage of the fact that ROMP of strained bicyclic dienes produces cyclopentene derivatives, analogous to the way bicyclic alkenes generate cyclopentane derivatives. This strategy results in the incorporation of the central ring of the DTE unit directly into the polymer backbone and produces high-content homopolymers (93 wt.-%) in good yield, with narrow polydispersities (1.3–1.4), and that display efficient photochromism both in solution and the solid-state (Figure 8). The high photochromic activity of these materials is facilitated by the polymer backbone, where the thiophene heterocycles are free to rotate in the material because they are not attached to the polymer backbone. This allows the DTE units to interconvert between the parallel and antiparallel conformation. Most noteworthy is the retention of the functional groups (“R”), which are the most useful when developing designer photoresponsive materials for specific applications. Because the thiophene heterocycles are not a part of the polymer's main-chain, the polymers can be decorated with a range of functional groups providing control of the electronic properties, the photochromic characteristics and the solubility. Both hydrophilic and lipophilic versions of the polymers have been prepared and tested. We are now investigating these materials as components in optoelectronic devices and will be reporting the results of these studies in due course.

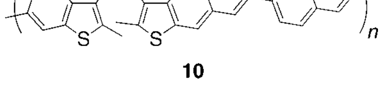

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Figure 7. A PPV-DTE copolymer.

Outlook

The goal of photochromic polymer research is to develop robust materials containing high concentrations of the photoactive components. In this report, we have presented several of the current approaches to construct high-content DTE homopolymers and copolymers. We have outlined the conformational aspects that should be considered when designing DTE polymers and have attempted to emphasize its importance. It is critical to have a polymeric architecture that is flexible enough to accommodate interconversion between the parallel and the productive antiparallel conformations. Alternatively a more rigid polymer can be constructed provided the polymer backbone forces the DTE units into the antiparallel conformer. Solutions to low photochromic activity in DTE polymers included copolymerizing with bulky side-groups or ring-closing the DTE units prior to polymerization.

The transition from solution to the solid-state is a critical step if photochromic technology is to be rendered useful in functional materials applications. This transition requires a solid understanding of molecular structure-function relationships as well as how these characteristics will translate when introduced into the macroscopic realm. Strong collaborations between skilled synthetic chemists and experienced materials scientists are essential in bridging this gap, and our research group is committed to this end.

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