Dendrimer diarylethenes: the memory effect of conformation in polymer matrices†

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Photochromic dendrimer diarylethenes with a C-2-connected bisbenzothienylethene core were synthesized; the most notable feature of them is the strong memory effect of cyclizable conformation of the open form when generated from the closed form by visible light irradiation in polycarbonate films.

A number of photochromic compounds have been synthesized to date.[1] Diarylethenes are some of the most promising photochromic compounds because of their high photochemical durability as well as their facile synthetic pathways.[2]

When a new photochromic compound is synthesized, its photochromic properties are always examined in solution first. However, when it becomes a candidate for applications, after required modifications of the structure to append functions it is usually shaped into the form of solid materials such as molecularly dispersed polymer films,[3] main chain polymer films,[4] pendant polymer films,[5] organic–inorganic hybrid polymer films,[6] amorphous films,[7] or crystals.[8]

However, solid state photochromism is sometimes retarded compared to solution photochromism. Thermally reversible photochromic compounds such as naphthopyrans have been widely used for auto light-regulating ophthalmic lenses.[1b] The speed of their decolouration reactions is expected to be fast in solid state materials. Evans and co-workers have demonstrated an attractive method for increasing the decolouration speed by preparing an oligosiloxane-based fluid environment around the photochromic molecules dispersed in polymer matrices.[9]

We have encountered a strong retardation of photochromic conversion to the coloured form (only a few percent) when **1**[10] (Chart 1) was placed, either as the O-form or as the C-form, in a polymer film. As the C-form generates the photocyclizable antiparallel O-form by visible light irradiation, it is apparent that there is no memory effect for the conformation of the **1O** molecules thus generated. We thought that this was caused by the interference of the polymer media with the molecule to fix its conformation making it unfavourable to cyclization.

Different from Evans' viewpoint, we tried to construct a bulky and thick shell at the outermost edge of the molecule, which prevents the invasion of the constraining polymer chains, in order to retain a soft and fluid environment around the photochromic core. We chose dendrimers to keep the photochromic properties of diarylethenes placed in polymer matrices like those in solution. We here report the photochromism of dendrimer diarylethenes in solution as well as the notable photochromic features in polymer matrices.

Dendrimers have been known as structurally well-defined tree-like polymers since the first synthesis of Tomalia and co-workers.[11] Not only because of their unique structure but also because of their peculiar properties, dendrimers are often applied to photochromic systems. Although several dendrimers of photochromic molecules have been synthesized,[12] only a series of dendrimers with a diarylethene core has been reported, with no information on their photochromic properties.[13] Therefore it is another interest to clarify the general photochromic properties of dendrimer diarylethenes.

We employed the aryl benzyl ether units for the convergent construction of a dendron that had been used successfully for azobenzene dendrimers.[12a] We also employed 1,3,5-trihydroxybenzene as the connecting agent of dendron and bisbenzothienylethene **2**.[3b] Accordingly, we synthesized the diarylethenes **3** (generation 0)–**7** (generation 4) from **2** (Chart 1).

GPC graphs (Fig. 1) of the diarylethenes **3–7** as their O-forms as well as the photostationary state (pss) under light irradiation at 366 nm in chloroform show that there is little difference in the retention time between the O-form and the pss. It means that the molecular shape and size did not change largely during the photocyclization.

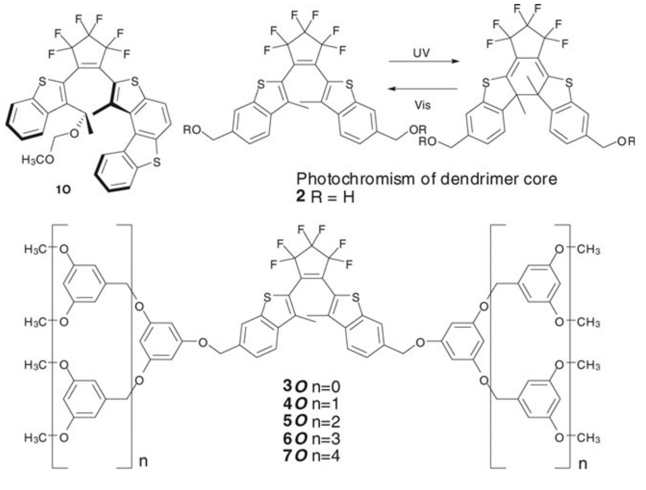

Chart 1

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† Electronic supplementary information (ESI) available: Synthetic details, ^{1}H NMR spectra, MALDI-TOF MS, photochromic reactions of **3–7**, and detailed analysis of the experimental results for **3–7**. See DOI: 10.1039/b812503a

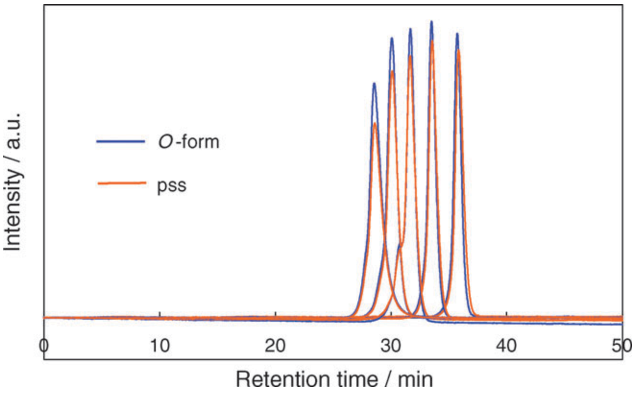

Fig. 1 GPC traces of diarylethenes **3–7** in chloroform.

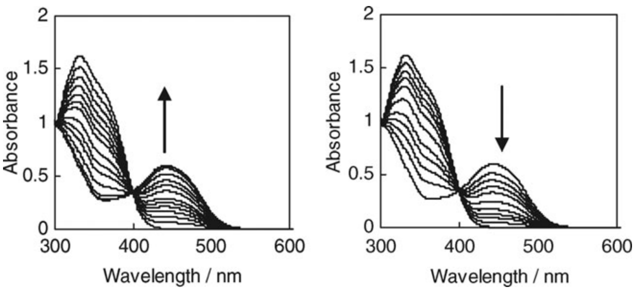

Fig. 2 Absorption spectral change in $CHCl_3$: (a) from **6O** to pss by 366 nm light; (b) from pss to **6O** by 477 nm light irradiation. Time interval: 15 s to 15 min. Concentration: 1×10^{-4} mol dm^{-3}.

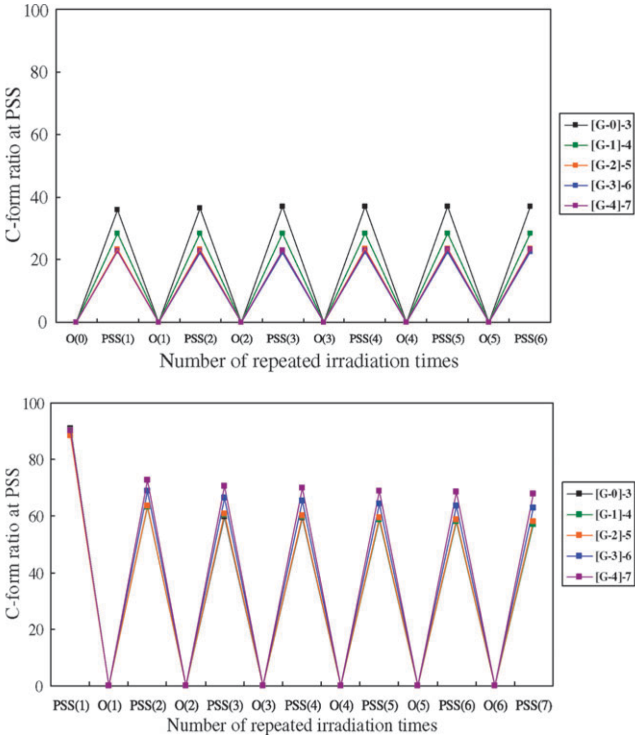

Fig. 3 Conversion ratio (CR) of dendrimer diarylethenes in polycarbonate film. Concentration: 3.4–4.4 × 10^{-3} mol dm^{-3}. Film thickness: 110–125 μm. (a) Started from O-form. (b) Started from pss prepared in $CHCl_3$.

All the dendrimer diarylethenes showed excellent photochromic performances in chloroform. For example, under irradiation of 366 nm light the chloroform solution of **6O** yielded pss (**6C** : **6O** = 91 : 9) (Fig. 2). Under irradiation of 477 nm light the pss solution was restored to the O-form. All the dendrimer diarylethenes showed excellent conversion to the C-form (*ca.* 90%), and neither side reactions nor thermal back reactions were observed. Their absorption spectral data and the quantum yields of photoreactions in chloroform are summarized in Table S1 in the ESI†.

We then examined the photochromic reactions of dendrimer diarylethenes in polycarbonate of bisphenol A (PC) films. The film thickness was 110–125 μm, and the concentration of the dendrimer diarylethenes was 3.4–4.4 × 10^{-3} mol dm^{-3}. When they were dispersed as their O-forms, the conversion ratios (CRs) to the coloured forms in PC films upon 366 nm light irradiation were merely 23–36% (Fig. 3a).

To the contrary, when they were dispersed in PC films in their pss under light irradiation at 366 nm in chloroform, the high conversion level was maintained for successive irradiation cycles, although the first visible-UV irradiation cycle decreased the CR from *ca.* 90% to *ca.* 60–70% (Fig. 3b).

These experimental data, shown in Table 1, were analyzed, and details of the analyzing processes are described in the ESI†.

The notable and striking features are: (1) the CRs are higher when incorporated as UV-pss (*i.e.* C-form) than incorporated as the O-form, and (2) the ratio of C-form generated from the "antiparallel O-form" which used to be the C-form in the UV-pss in $CHCl_3$, was higher for later generation dendrimers (*e.g.*

Table 1 Photochromic conversion data for dendrimer diarylethenes

		In PC film				
			Mixed as UV-pss generated in $CHCl_3$			
	CR in $CHCl_3$	CR when mixed as **O**	CR after 1st cycle	Ratio of **C** to **O** initially mixed as **O** of pss after 1st cycle	Ratio of **C** to **O** initially mixed as **C** of pss after 1st cycle	Ratio of **C** to "antiparallel **O**" generated from **C** of pss after 1st cycle
3	0.91	0.36	0.63	0.032	0.60	0.66
4	0.91	0.28	0.63	0.025	0.60	0.66
5	0.89	0.23	0.64	0.025	0.61	0.69
6	0.91	0.23	0.69	0.021	0.67	0.74
7	0.91	0.23	0.73	0.021	0.71	0.78

[a] CR: conversion ratio at UV-pss to the C-form.

66% for **3** but 78% for **7**: see ESI† for derivation and calculation). These can be best explained as follows: (1) the dendrons act as the anchor to fix the molecular conformation that the molecule takes when incorporated in the polymer matrix, and (2) the larger dendron can secure the fluidity of the antiparallel diarylethene core part inside the dendrimer by blocking the interference of the surrounding polymer media, so that the molecule can have enough room to change structure during the formation of the new C–C single bond at the excited state.

In conclusion, we have synthesized dendrimer diarylethenes and clarified their excellent photochromism in solution. When they are placed in polymer media, we have succeeded in keeping the fluidity of the photochromic core by preparing a thick wall of dendron at the outermost edge of the molecule and consequently succeeded in keeping the high conversion ratio to the C-form by introducing the dendrimer diarylethenes into the polymer matrices as their photostationary states of UV irradiation in solution. The conversion ratio was higher when the generation of the dendrimer is later.

The dendrimer protocol to fix the antiparallel conformation must be useful when highly functionalized diarylethenes will be used as organic photoresponsive materials in polymer matrices.

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