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Pseudopolyrotaxane composed of an azobenzene polymer and γ-cyclodextrin. Reversible and irreversible photoisomerization of the azobenzene groups in the polymer chain

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A polyrotaxane composed of γ-cyclodextrin and azobenzene containing polyester undergoes UV light induced isomerization of *trans*- to *cis*- azobenzene, whereas the reverse isomerization does not occur under the usual conditions of irradiation with visible light.

Interactions of various compounds with photoisomerizable azobenzene groups with cyclodextrins have been investigated to develop new photoresponsive materials.[1] Much attention has been directed toward cyclodextrin-based polyrotaxanes and pseudopolyrotaxanes of azobenzenes.[2] Recently, a rotaxane system composed of cyclodextrin (CD) and an azobenzene-containing polymer exhibited quick and reversible molecular shuttle type behavior induced by photoisomerization of the azobenzene group.[3] In the course of our study of the preparation and properties of various pseudopolyrotaxanes with cyclodextrins,[4] we observed a significant influence of the host CD molecules on the photoinduced *cis–trans* isomerization of the azobenzenes. Here we report syntheses of a new pseudopolyrotaxane of polyazobenzene and of a corresponding CD free polyazobenzene, as well as the effect of CD on the photoisomerization of polyazobenzene.

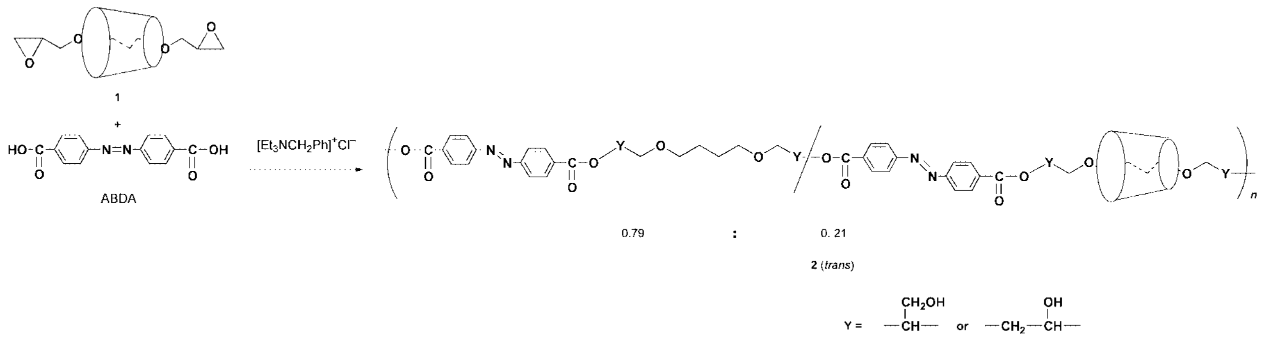
A 1 : 1 inclusion complex of butane-1,4-diol diglycidyl ether (BDGE) [1,4-bis(2,3-epoxypropoxy)butane] and γ-CD (**1**)[5] reacts with azobenzene-4,4′-dicarboxylic acid (ABDA) in the presence of a catalytic amount of $[Et_3NCH_2Ph]^+Cl^-$ to afford the pseudopolyrotaxane **2**(*trans*), which, on average, contains 0.21 γ-CD unit per repeating unit as evaluated from elemental analysis and NMR spectroscopy (Scheme 1). The azobenzene groups in the polymer take the *trans* configuration, as revealed by UV-vis spectroscopy. The pseudopolyrotaxane **2**(*trans*) gives a DSC scan which is quite different from that of a physical mixture of **2**(*trans*) and γ-CD. Analysis by GPC gives values for M_n of 9500 and M_w of 17 100 (*vs.* polystyrene standards).

Cyclodextrin-free polyester (**3**(*trans*)) having azobenzene groups with M_n = 8750 and M_w = 15100 was also obtained as an orange solid (76%) in a similar fashion from the polyaddition of BDGE to ABDA (Scheme 2). The ratio of $-CH(CH_2OH)-$ and $-CH_2-CH(OH)-$ linkages formed *via* α- and β-cleavage of the oxirane ring, respectively, is determined to be 0.62 : 0.38. Similar ratios have been reported for polymers obtained by the ring-opening polyaddition of diglycidyl ethers and dicarboxylic acids.[6] An attempt to prepare **2**(*trans*) from a mixture of γ-CD and **3**(*trans*) was not successful, indicating that the polymers, once formed, do not form the supramolecular system with γ-CD, presumably due to the presence of the bulky azobenzene units.

Photoisomerization of the azobenzene group[7] of **2**(*trans*) and **3**(*trans*) was investigated, and the results were compared. Upon irradiation of a DMSO solution of **2**(*trans*) with UV light (245 nm), the absorption peak at 331 nm due to the π–π* transitions of the *trans* azobenzene unit decreased accompanied by growth of the peak at 433 nm due to the n–π* transition of the *cis* azobenzene unit.[8] Fig. 1 shows changes in the absorption spectrum during the reaction, which follows first-order kinetics with a rate constant of 1.7×10^{-3} s^{-1} at 30 °C and 1.5×10^{-3} s^{-1} at 25 °C. The γ-CD free polyester **3**(*trans*) undergoes a similar *trans* to *cis* photoisomerization under irradiation with UV light (245 nm) and gives a first-order rate constant (1.3×10^{-3} s^{-1}, 25 °C) comparable to that of **2**(*trans*). These results clearly indicate the occurrence of the photoinduced isomerization of **2**(*trans*) and **3**(*trans*) to **2**(*cis*) and **3**(*cis*), respectively.

As for **3**(*cis*), irradiation with visible light ($>$ 440 nm) causes a reverse isomerization, increasing the strength of the peak at 330 nm and decreasing the strength of the peak at 432 nm. It has been reported that various azobenzenes undergo a similar reverse photoisomerization under irradiation with visible light. However, irradiation of the DMSO solution of **2**(*cis*) with visible light ($>$ 440 nm) caused no observable isomerization of **2**(*cis*) to the original **2**(*trans*). Heating of **3**(*cis*) at 50 °C also leads to its isomerization to **3**(*trans*) within 15 min, whereas **2**(*cis*) does not undergo such thermally induced isomerization. Since **2** and **3** have similar molecular weights and polydispersities, the large difference in the photo and thermally induced isomerization may be ascribed to a difference in the molecular structure or aggregation behavior between **2** and **3** in solution.

Fig. 2 shows plots of η_{sp}/c against c for **2**(*trans*), **3**(*trans*), **2**(*cis*), and **3**(*cis*). As shown in Fig. 2, **2**(*cis*) gave a larger η_{sp}/c value and a larger slope in the η_{sp}/c *vs.* c plots, compared with



Scheme 1

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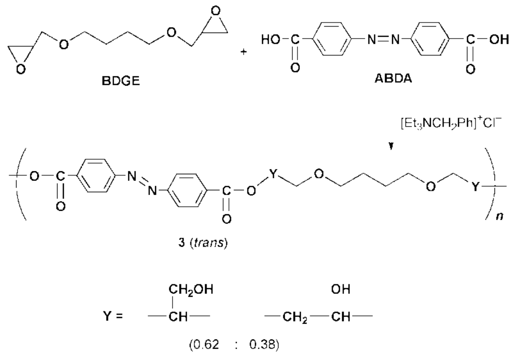
the other three polymers. The larger slope suggests the presence of intermolecular interactions between the polymer molecules. On the other hand, for polyamide type polyazobenzenes –(amide unit–N=N–)$_n$–, it is reported that the *cis* and *trans* polymers give the same slope in the η_{sp}/c *vs.* c plots.[9] In this case, photoinduced *cis* to *trans* isomerization proceeds smoothly. The viscometric results of **2**(*cis*) suggest the presence of significant intermolecular interactions between **2**(*cis*) molecules assisted by CD, which may effect the *cis* to *trans* isomerization of the azobenzene group. Chart 1 depicts a schematic drawing of intermolecular interactions between the pseudopolyrotaxane molecules caused by N···H–O hydrogen bonds. The *cis* azobenzene group is sterically less crowded and has a higher proton affinity than the *trans*-azobenzene groups. By forming the hydrogen bond, the cis form of azobenzene seems stabilized. Addition of large excess amounts of γ-CD to a DMSO solution of **3**(*cis*) retards the photoinduced *cis* to *trans* isomerization, but γ-CD contained in **2** (0.21 molarity of the monomer units) blocks the isomerization much more effectively. This may also be due to stabilization of the *cis*-azobenzene unit by hydrogen bonding with γ-CD. The retardation effect appears to be more effective in **2**(*cis*) which has the γ-CD unit in its own polymer chain.



Scheme 2

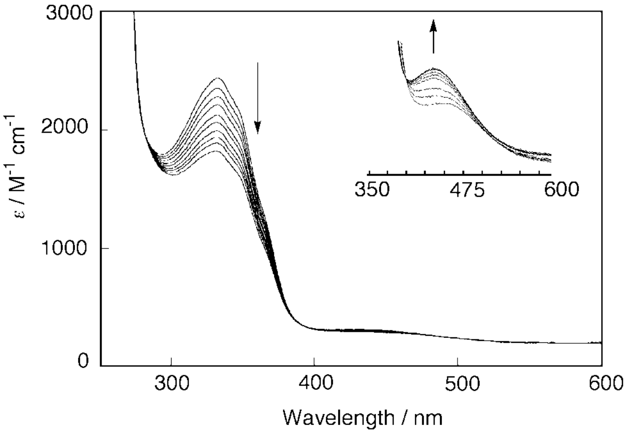


Fig. 1 Change of the absorption spectra of DMSO solution of **2** during isomerization from the *trans* to the *cis* form irradiated with UV light (245 nm) at 30 °C. The spectra were recorded at t = 0, 2, 4, 6, 8, 10, 12, 14, 16 and 18 min.

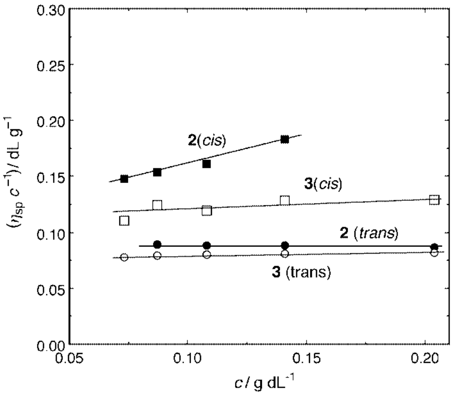
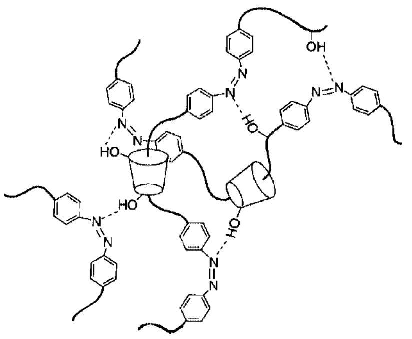


Fig. 2 Viscosity of **2**(*trans*) and **3**(*trans*) in DMSO at 25 °C before and after irradiation with UV light (245 nm).



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