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Effect of α-Cyclodextrin on the Photoisomerization of Azobenzene Functionalized Hydroxypropyl Methylcellulose in Aqueous Solution

Weiyan Wang, Ming-Zhu Wang (✉)

The 13th Research Institute of China Electronics Technology Group Corporation, 113 Hezuo Road, Shijiazhuang, 050051, P. R. China
Hebei University of Science and Technology, 050018, Shijiazhuang, P. R. China
E-mail: wangmz666@126.com

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Summary

The effect of α-cyclodextrin (α-CD) on the *trans-cis* photoisomerization of an azobenzene functionalized polymer (AZO-HPMC) in aqueous solutions has been systematically studied. It has been shown that the *cis* fraction at the photostationary states and the photoisomerization rate constant increases with increasing α-CD concentration, indicating that the *trans-cis* photoisomerization of AZO-HPMC is accelerated by addition of α-CD. This behavior is interpreted in terms of the aggregation between the azobenzene groups. The formation of inclusion complexes between the *trans* isomers and α-CD inhibits the aggregation and consequently increases the mobility and free volume for the isomerization.

Keywords

cyclodextrin, azo-polymer, photoisomerization

Introduction

Photoisomerization of azobenzene-containing polymers have been extensively investigated by many researchers. It has been shown that the isomerization of azo polymers depends not only on the chemical structure of the azobenzene chromophores but also on the properties of polymer matrixes[1,2].
Cyclodextrins (CDs) are well known in supermolecular chemistry as molecular hosts [3,4]. They can selectively form inclusion complexes with a variety of guest molecules in aqueous solution. Molecules containing azobenzene moieties can also form inclusion complexes with CDs[5-10]. It has been proven that *trans* azobenzene forms stable inclusion complexes with α-CD, while *cis* azobenzene does not form any inclusion complex with α-CD[8]. This suggests that the change in the geometry of azobenzene plays an important role in the formation of inclusion complexes between CDs and azobenzene compounds. CDs are shown to have significant effects on the *trans-cis* isomerization of low molecular weight azobenzene compounds[6,9,10].

Sawada et al[6] found that when a methyl orange molecule forms complex with two CD molecules from both sides (1:2 complex), the photoisomerization is slowed down and the yield of *cis* isomer (similar to f_Z in this study) decreases by 30% compared to that of the 1:1 complex, indicating a confinement effect of CDs. Botolus and Monti[9] reported that the quantum yields of the *trans-cis* photoisomerization of azobenzene inclusion complexes with α-CD in aqueous solution are significantly lower than that of "free" azobenzene in a water/methanol (80/20, v/v) medium. They attributed this decrease to constrained molecular motion of azobenzene in the inclusion complexes.

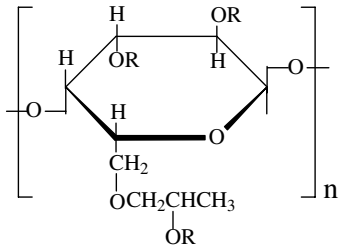
Ikeda et al [11] studied the pseudo-polyrotaxane formation between α-CD and azobenzene-terminated poly(ethylene glycol) (azo-PEG-azo). It was found that when the terminal azobenzene groups are in the *trans* state, α-CD can thread into the middle PEG block to form pseudo-polyrotaxane; but when both terminal azobenzene groups are in the *cis* state, the pseudo-polyrotaxane formation was hindered. Rodriguez-Cabello et al. [12] reported the inclusion complexation behavior between an azobenzene modified elastin-like polymer poly(VPGVG) and α-CD. They showed that the phase behavior of this azo-polymer can be inversely controlled by photoirradiation and the addition of α-CD. However, there is no report on how CDs affect the isomerization of azo polymers.

In this paper, the effect of α-CD on the *trans-cis* photoisomerization of an azobenzene functionalized polymer in aqueous solutions has been systematically studied. It has been shown that the *trans-cis* photoisomerization of this azo-polymer is accelerated by addition of α-CD. This study provides important insight into the isomerization mechanism as well as the inclusion complexation behavior of azo-polymers in aqueous solutions.

Experimental

Materials

AZO-HPMC polymers with different degrees of azo-subsitution (DS_{azo}) were prepared by esterification reaction of the hydroxyl groups on HPMC (Metolose 90SH100, DS=1.4, MS=0.2) with 4-phenylazobenzoyl chloride. The preparation and characterization of these polymers have been reported previously[13]. The structure of AZO-HPMC is illustrated in Scheme-1. Aqueous solutions of AZO-HPMC were prepared using deionized water and cooled below 5°C. α-CD (98%) was obtained from Fluka and used as received.



R = H, CH_3, or OC–⟨⟩–N = N–⟨⟩

Scheme-1: Chemical structure of AZO-HPMC

Equipments

Photoirradiation was carried out with a 500 W Hg ARC lamp (Oriel, Model 68910) at 25°C in a dark room. The exposure energy of irradiation was about 2 mW/cm^2. UV and visible light were isolated by 370 nm and 410 nm interference filters respectively. A quartz cell containing the sample solution was irradiated with visible light for 20 min and then kept in a dark room for 72 hours to obtain the dark-adapted samples. UV-irradiated samples were obtained by irradiating the dark-adapted samples with UV light for different times.

A Shimadzu UV-2501PC Spectrophotometer was used to study the effect of α-CD on the *trans-cis* isomerization of AZO-HPMC. The absorption spectra were recorded in the range of 200-600 nm.

Results and Discussion

Figure-1 shows the UV-visible absorption spectra of AZO-HPMC (DS_{azo} = 0.018) in aqueous solution (0.4 g/L) after irradiation with UV light, and subsequent irradiation with visible light. At room temperature, azobenzene chromophores are expected to be in the more stable *trans* state in the dark. Under these conditions, the absorption spectrum of AZO-HPMC shows a major absorption peak at 326 nm and a weak one at 435 nm, which are assigned to the π-π* electronic transition of the *trans* isomers and n-π* transition of the *cis* isomers, respectively. Upon irradiation with UV light, AZO-HPMC undergoes *trans-cis* photoisomerization. The intensity of the absorption peak at 326 nm progressively decreases with increasing irradiation time until an equilibrium state is reached. At the same time, the weak peak at 435 nm becomes more pronounced. The equilibrium or photostationary state (in this study, the photostationary state indicates the equilibrium state after UV irradiation unless otherwise stated) is reached in about 1200 seconds under the irradiation conditions used in this experiment.

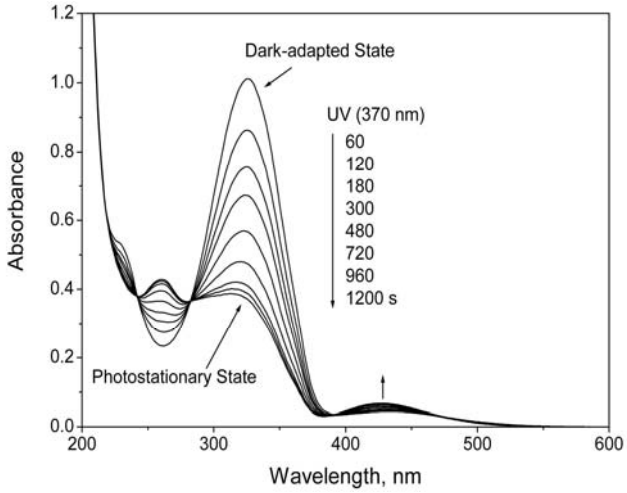


Figure-1: UV-vis absorption spectra for the *trans-cis* photoisomerization of AZO-HPMC aqueous solution (DS_{azo}=0.018, 0.4 g/L). Light intensity, UV: 2 mW/cm^2, Vis: 3 mW/cm^2

Similar behavior was also observed for aqueous solutions of AZO-HPMC in the presence of α-CD. A typical example is shown in Figure-2. In the presence of 4.0 mM α-CD, the π-π* absorption of *trans* isomers and the n-π* absorption of *cis* isomers red shifts to 333 nm and 440 nm, respectively. Moreover, at the photostationary state, the π-π* absorption of *trans* isomers is relatively lower, while the n-π* absorption of *cis* isomers is higher than that in the absence of α-CD.

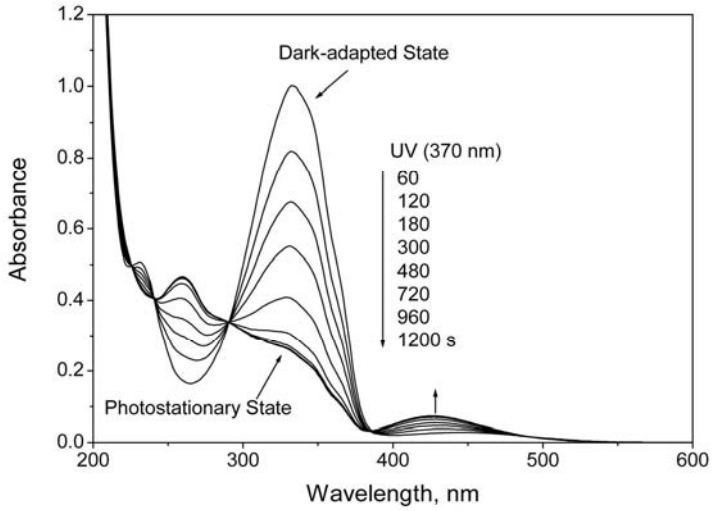


Figure-2: UV-Vis absorption spectra for the *trans-cis* photoisomerization of AZO-HPMC aqueous solution (DS_{azo}=0.018, 0.4 g/L) in the presence of 4.0 mM α-CD. Light intensity, UV: 2 mW/cm^2, Vis: 3 mW/cm^2

When the *trans* isomers with an initial concentration $[E]_0$ are irradiated with UV light, the rate of change in the concentration of *trans* isomers at time *t*, $d[E]_t/dt$, is given by equation (1).

$$-d[E]_t / dt = k_1[E]_t - k_2[Z]_t - k_3[Z]_t \quad (\mathbf{1})$$

where k_1, k_2 and k_3 are the rate constants for the *trans-cis* photoisomerization, *cis-trans* photoisomerization and *cis-trans* thermal isomerization respectively, $[E]_t$ and $[Z]_t$ are the concentrations of *trans* and *cis* isomers, which can be calculated using equation (2):

$$[Z]_t = [E]_0 - [E]_t \quad (\mathbf{2})$$

The fraction of the *cis* isomers at irradiation time *t*, $f_Z(t)$, can be calculated from the absorbance *A* at λmax of the π-π* absorption of *trans* isomers at time *t* by equation (3) [14,15].

$$f_Z(t) = \frac{[Z]_t}{[E]_0} = \frac{1 - A_t / A_0}{1 - \varepsilon_Z / \varepsilon_E} \quad (\mathbf{3})$$

where A_0 is the initial absorbance of *trans* isomers, A_t is the absorbance at time *t*, ε_E and ε_Z are the extinction coefficients of *trans* and *cis* isomers. $\varepsilon_E/\varepsilon_Z$ is calculated to be

0.05 using the method developed by Fischer[16]. This value is in agreement with reported values of 0.055 for amphiphilic polyelectrolytes containing azobenzene moieties[14].

The rate constant k_1, for the *trans-cis* photoisomerization is given by equation (4)[17]:

$$(1-\frac{A_S}{A_0})\ln(\frac{A_0-A_S}{A_t-A_s}) = k_1 t \qquad (\mathbf{4})$$

where A_S is the absorbance at the photostationary state.

The changes of absorbance as a function of irradiation time for the *trans-cis* photoisomerization of AZO-HPMC (DS_{azo}=0.018, 0.4 g/L) in the presence of different amounts of α-CD upon irradiation of 370 nm UV light (2 mW/cm^2) are shown in Figure-3. It can be seen that the absorption curves of AZO-HPMC in the presence of α-CD significantly deviate from the curve in the absence of α-CD, although they all follow similar decreasing trends. This indicates that α-CD have significant effects on the *trans-cis* photoisomerization of AZO-HPMC in aqueous solutions.

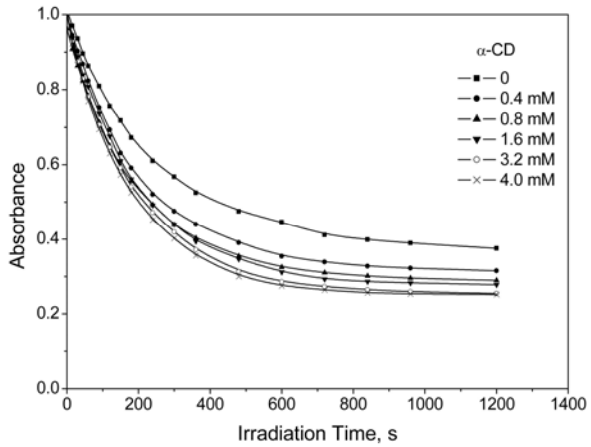


Figure-3: Changes of absorbance as a function of irradiation time for the *trans-cis* photoisomerization of AZO-HPMC (DS_{azo}=0.018, 0.4 g/L) in the presence of α- CD upon irradiation of 370 nm UV light (2 mW/cm^2)

The changes of *cis* fraction as a function of irradiation time for AZO-HPMC (DS_{azo} = 0.018, 0.4 g/L) in aqueous solutions in the presence of different amounts of α-CD are presented in Figure-4. Irradiation beyond 1200 seconds does not lead to further increase in the *cis* fraction, indicating that the photostationary state is reached. The first-order plots for the *trans-cis* photoisomerization of AZO-HPMC in the presence of different amounts of α-CD are presented in Figure-5. In each case, the *trans-cis* photoisomerization process follows first-order kinetics in the whole time range investigated. The data of f_Z and k_1 are summarized in Table-1. It can be seen that both f_Z and k_1 increase with increasing α-CD concentration, showing that the *trans-cis* isomerization process of AZO-HPMC is enhanced. This behavior is due to the destruction of azobenzene aggregates upon addition of α-CD. A schematic illustration of this effect is given in Scheme-2 and discussed in detail as below.

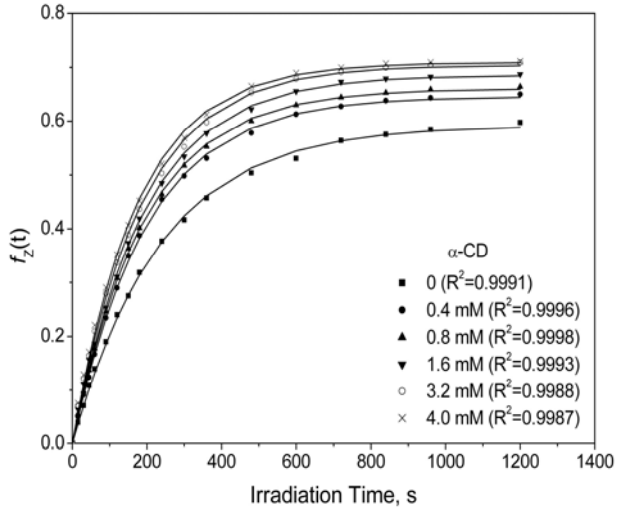


Figure-4: Changes of *cis* fraction as a function of irradiation time for the *trans-cis* photoisomerization of AZO-HPMC (DS_{azo}=0.018, 0.4 g/L) in the presence of α-CD upon irradiation of 370 nm UV light (2 mW/cm^2)

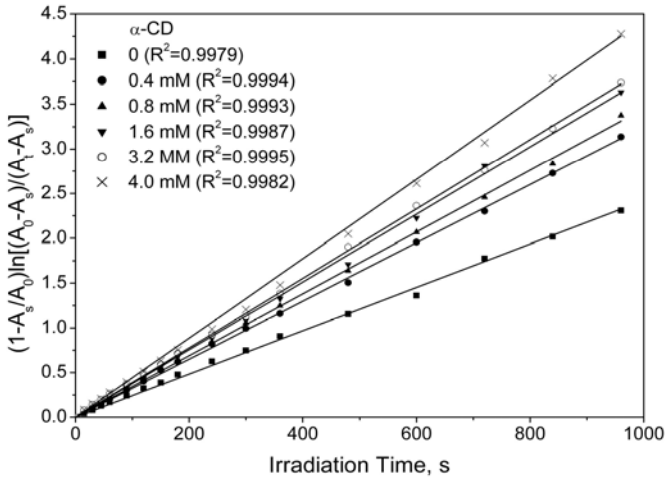


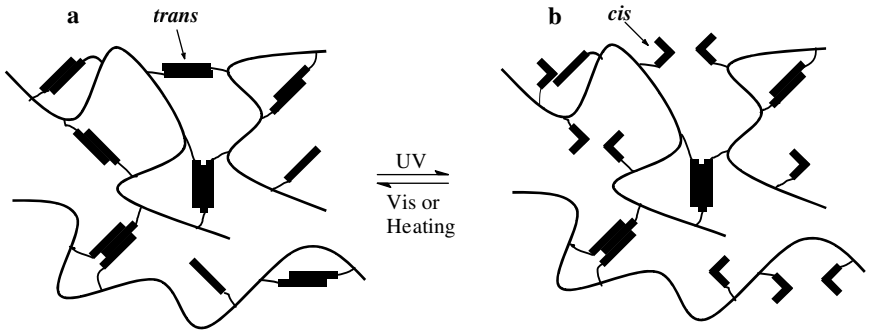
Figure-5: First-order plots for the *trans-cis* photoisomerization of AZO-HPMC (DS_{azo}=0.018, 0.4 g/L) in the presence of α-CD upon irradiation of 370 nm UV light (2 mW/cm^2)

When azobenzene moieties in AZO-HPMC are in the more planar *trans* configuration, Aggregates are readily formed as a consequence of self-association of the azobenzene groups (Scheme 2a). The aggregates restricts the movement of azobenzene moieties and hinders the *trans-cis* isomerization of AZO-HPMC. On the other hand, since the *cis* isomers are bulkier than the *trans* isomers, the *trans-cis* isomerization requires free volume (127 Å^3). When azobenzene moieties form aggregates, the free volume available for the configuration change reduces compared to the unassociated azobenzene molecules (Scheme 2b). In this case, the *trans-cis* photoisomerization becomes more difficult due to the steric hindrance effect of the neighboring

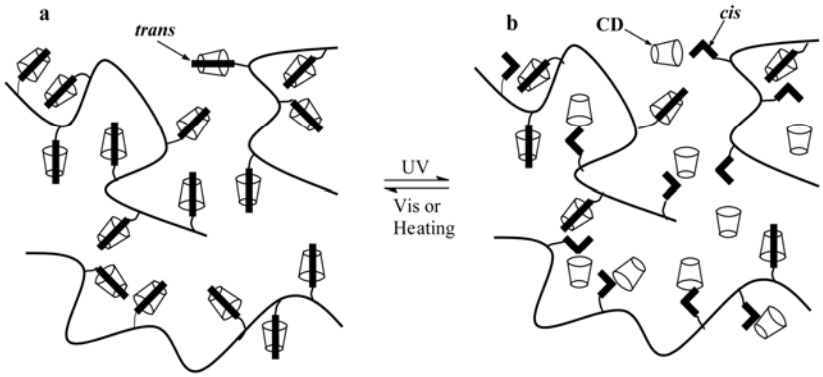
Table-1: Characteristics of the photoisomerization of AZO-HPMC (DS_{azo}=0.018, 0.4g/L) in the presence of α-CD upon irradiation of 370 nm UV light (2 mW/cm^2)

α-CD Concentration (mM)	*Cis* fraction at the photostationary state f_Z (%)	Rate constant for the *trans-cis* photoisomerization k_1 ($s^{-1}\times10^{-3}$)
0	59.3	2.42
0.4	64.6	3.25
0.8	66.1	3.45
1.6	68.6	3.78
3.2	70.5	3.88
4.0	70.9	4.37

azobenzene groups. However, in the presence of α-CD, the *trans* isomers form inclusion complexes with α-CD, which inhibits the aggregation of azobenzene groups (Scheme-3a). In this case, the free volume around the azobenzene groups is expanded and the steric hindrance effect of the neighboring azobenzene groups no longer exists. Therefore, the *trans-cis* photoisomerization process is accelerated, and more *trans* isomers are converted to the *cis* isomers due to the "liberation" of azobenzene groups from the aggregates (Scheme-3b).



Scheme-2: Schematic illustration of the *trans-cis* isomerization of AZO-HPMC in aqueous solution



Scheme-3: Schematic illustration of the effect of α-CD on the *trans-cis* isomerization of AZO-HPMC in aqueous solution

It should be noted that the formation of inclusion complexes with α-CD also reduces the mobility of azobenzene groups in view of the fact that *cis* isomers of azobenzene groups are unable to form inclusion complexes with α-CD due to its steric hindrance. In other words, during the *trans-cis* photoisomerization, the *trans* isomers have to be excluded from the cavity of α-CD in order to convert to the *cis* isomers. Since the complexes are stable, the interactions between the azobenzene groups and the cavity of α-CD is strong, the exclusion of the *trans* isomers from the cavity of α-CD would be unfavorable from a thermodynamic point of view. This confinement effect may hinder the *trans-cis* photoisomerization of AZO-HPMC. However, as compared to the α-CD's effect of increasing free volume by destructing the aggregates, the confinement effect of α-CD could be a less important factor for the photoisomerization. Taking into account the molecular dimensions of α-CD and azobenzene, it is easy to understand the above discussion. Note that the required free volume for the *trans-cis* isomerization of azobenzene is estimated to be 127 $Å^3$, while the cavity volume of α-CD are approximately 174 $Å^3$. Although the cavity volume of α-CD is larger enough for the *trans-cis* isomerization of azobenzene, the internal cavity diameter of α-CD (4.7-5.3Å) is smaller than the dimension of *cis* azobenzene (5.5Å). Therefore, the *trans-cis* isomerization of azobenzene groups can only take place when the *trans* azobenzene groups are excluded from the cavity of α-CD.

Conclusion

α-CD inhibits the azobenzene aggregates of AZO-HPMC in aqueous solution and increases the mobility and free volume for the isomerization, which accelerates the trans-cis photoisomerization. Both the cis fraction at the photostationary states and the photoisomerization rate constant k1 increase with increasing α-CD concentration.

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