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Contrast Viscosity Changes upon Photoirradiation for Mixtures of Poly(acrylic acid)-Based α-Cyclodextrin and Azobenzene Polymers

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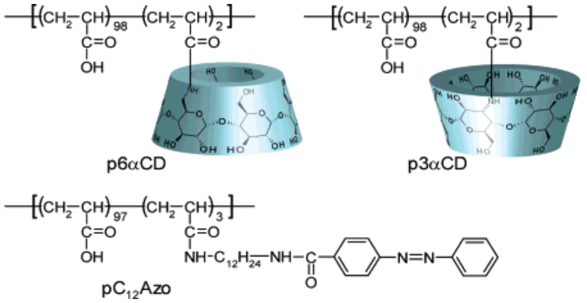
Stimuli-responsive self-assembling systems have attracted much interest from researchers because of their potentials in a broad range of fields, such as drug delivery systems, sensor systems, and functional nanodevices.[1] Cyclodextrins (CDs) are a promising material for construction of stimuli-responsive self-assembling systems.[2] Recently, in the course of our study of molecular recognition of CDs with polymer side chains,[3,4] we have successfully constructed a photoresponsive hydrogel system using molecular recognition by combination of α-CD, dodecyl-modified poly(acrylic acid), and a photoresponsive competitive guest.[5] To expand the photoresponsive system to a polymer−polymer interaction system, we designed poly(acrylic acid)s (pAA) carrying CD moieties (p3αCD and p6αCD) and a pAA carrying azobenzene moieties ($pC_{12}Azo$), as shown in Chart 1, and investigated the detail of the interactions of these polymers by several techniques, including steady-shear viscosity (η) measurements and NMR. In this communication, we report contrast η changes upon photoirradiation for the p3αCD/pC_{12}Azo and p6αCD/pC_{12}Azo mixtures.

The interaction of the CD polymers with pC_{12}Azo was investigated by η measurements under semidilute conditions because the formation of inclusion complexes of CD moieties in the CD polymers with side chains of guest polymers may lead to an increase in solution viscosity.[4,6] The η values for the p3αCD/pC_{12}Azo and p6αCD/pC_{12}Azo mixtures (6.5×10^{-1} and 2.5×10^{2} Pa•s, respectively) are larger than that for the pAA/pC_{12}Azo mixture (8.4×10^{-2} Pa•s). The η value for the p6αCD/pC_{12}Azo mixture is 2 orders of magnitude larger than that for the p3αCD/pC12Azo mixture, although both mixtures employ the same host−guest pair. The difference in η values corresponds to the difference in association constants (K): apparent K values were estimated to be $(1.4 \pm 0.2) \times 10^{2}$ and $(1.2 \pm 0.1) \times 10^{4}$ M^{-1} for the p3αCD/pC_{12}Azo and p6αCD/pC_{12}Azo systems, respectively, by UV−visible absorption spectroscopy (see Figure S1 in Supporting Information).

Since azobenzene derivatives are isomerized from *trans* to *cis* and from *cis* to *trans* under irradiation with UV and visible light, respectively,[7] we studied η change upon photoirradiation for the p3αCD/pC_{12}Azo and p6αCD/pC_{12}Azo mixtures. As shown in Figure 1, these mixtures exhibited contrast η changes upon photoirradiation. Upon photoirradiation with UV light, η decreases by nearly an order of magnitude in the case of the p3αCD/pC_{12}Azo mixture, whereas η increases about 2-fold in the case of the p6αCD/pC_{12}Azo mixture. On the other hand, upon subsequent photoirradiation with visible light, η values became similar before the UV irradiation for both the mixtures, respectively. These contrasting photoresponsive η changes occur repetitively upon successive irradiation of UV and visible light (Figure 1). Since ^{1}H NMR spectroscopy has confirmed that the contents of *trans*- and *cis*-Azo moieties are similar for both the p3αCD/pC_{12}Azo and p6αCD/pC_{12}Azo mixtures before and after photoirradiation with UV light (see Figure S2 in Supporting Information), the contrasting photoresponsive η changes may not be caused by the difference in efficiencies of photoisomerization of Azo moieties.

Chart 1. Structures of the Chemicals Used in This Study



NOESY spectra were measured to explore how CD moieties in the CD polymers interact with pC_{12}Azo before and after photoirradiation with UV light. The NOESY spectrum for the p3αCD/pC_{12}Azo mixture before UV irradiation demonstrated correlation peaks between inner protons in the CD moieties and protons due to both Azo and C_{12} moieties (Figure S3a in Supporting Information), indicating that CD moieties in the CD polymers interact not only with the Azo moiety but also with the C_{12} linker. The spectrum for the p3αCD/pC_{12}Azo mixture after UV irradiation exhibited only weak correlation peaks between protons due to the CD moiety and protons in the Azo and C_{12} moieties (Figure S3b). On the other hand, in the NOESY spectrum for the p6αCD/pC_{12}Azo mixture before UV irradiation, the correlation peak between protons due to CD and C_{12} moieties was much stronger than that between CD and Azo moieties (Figure 2a), indicating that the CD moiety in p6αCD interacts with the C_{12} linker much more favorably than with the Azo moiety. The spectrum for the p6αCD/pC_{12}Azo mixture does not show significant correlation peaks between protons due to the CD and Azo moieties, but it shows correlation peaks between

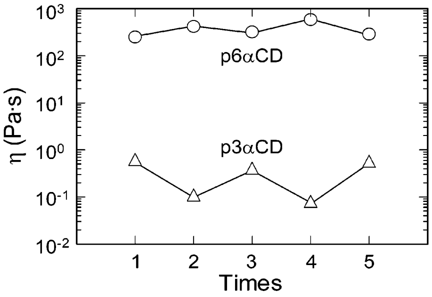


Figure 1. Changes in η for mixtures of p6αCD/pC_{12}Azo (circle) and p3αCD/pC_{12}Azo (triangle) after repetitive irradiations with UV and visible light.

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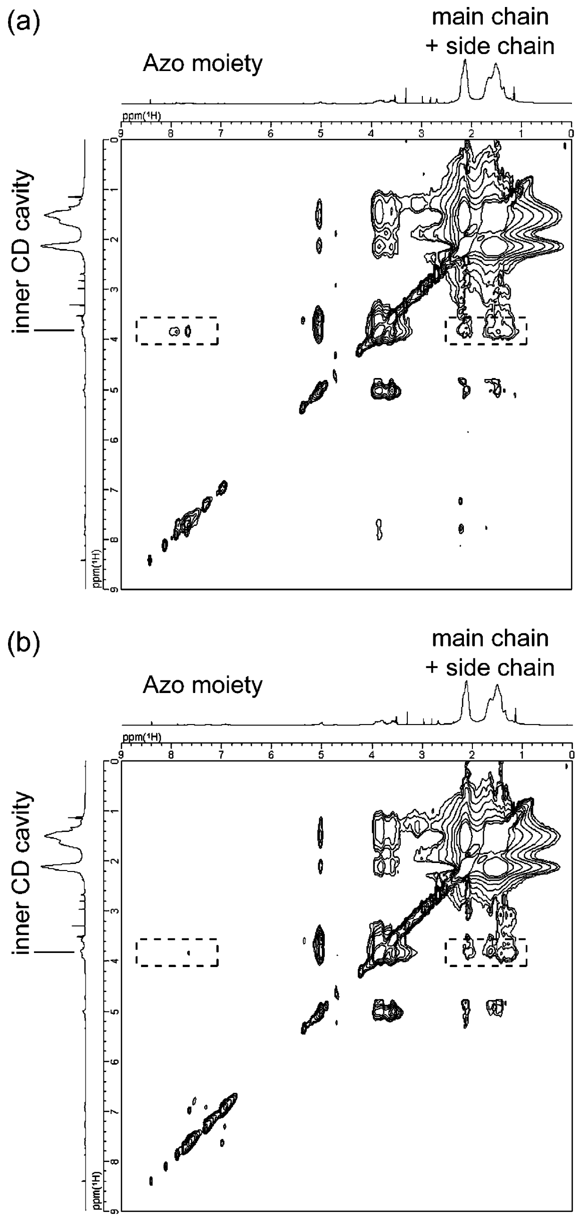
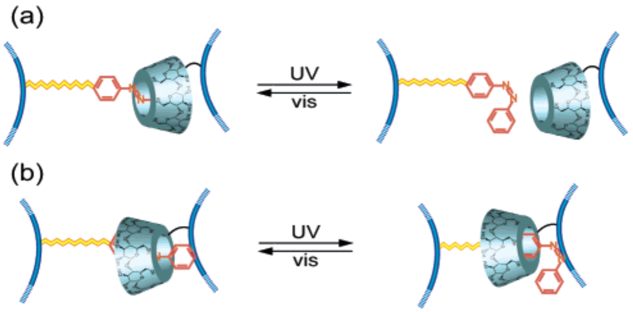


Figure 2. Two-dimensional NOESY spectra of 10 g/L pC_{12}Azo solutions in the presence of 15 g/L p6αCD measured before (a) and after (b) UV irradiation.

CD and C_{12} moieties (Figure 2b). These NOESY spectra indicate that photoirradiation with UV light causes dissociation of inclusion complexes for the p3αCD/pC_{12}Azo mixture, and it causes the formation of interlocked complexes for the p6αCD/pC_{12}Azo mixture (Scheme 1).

The η and NOESY data described above led us to conclude that the contrast η changes upon photoirradiation were ascribable to the difference in how CD moieties in the CD polymers interact with pC_{12}Azo after photoisomerization. For both the mixtures in the *trans*-Azo state (i.e., before irradiation with UV light or after irradiation with visible light), CD moieties interact with C_{12}Azo moieties to form inclusion complexes. For the p3αCD/pC_{12}Azo system in the *cis*-Azo state (i.e., after UV irradiation), the inclusion complexes are predominantly dissociated, resulting in the considerable η decrease. Also, for the p6αCD/pC_{12}Azo system, interlocked complexes are formed in the *cis*-Azo state, resulting in the slight η increase.

Scheme 1. Schematic Representation for Interactions of CD and Azo Moieties upon Irradiation with UV and Visible Light for p3αCD/pC_{12}Azo (a) and p6αCD/pC_{12}Azo (b)



Now we are studying the viscoelastic properties of the mixtures and the effect of the length of the alkyl chain connecting the main chain and the Azo moiety.

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Supporting Information Available: Preparation of polymers used, Benesi−Hildebrand plots for the mixtures, change in ^{1}H NMR, 2D NOESY spectra, and shear rate dependence of steady-shear viscosities. This material is available free of charge via the Internet at http://pubs.acs.org.

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