Complex Formation and Gelation between Copolymers Containing Pendant Azobenzene Groups and Cyclodextrin Polymers

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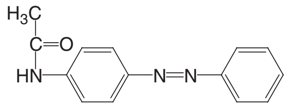
The copolymers of acrylamide and acrylamide with pendant azobenzene (AzBA–AAm) were prepared by radical polymerization. The association constants of *trans*-AzBA–AAm copolymers with β-CD are larger than those of *cis*-AzBA–AAm copolymers. The *trans*-AzBA–AAm guest copolymer was found to form supramolecular gels with β-CD–pAA (pAA; poly(allylamine)) host copolymers in water.

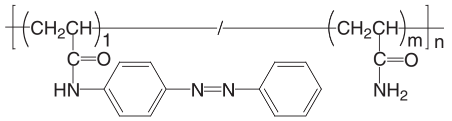
Specific recognition of substrates by enzymes, precise replication of DNA, and folding of proteins in biological systems play an important role in constructing supramolecular structure, achieving functions, and maintaining their lives.[1] Recently, the structures of various biological structures, such as RNA polymerase, DNA polymerase and λ-exonuclease, have been determined by X-ray crystallography and these enzymes have the cylindrical cavity in the substrate-binding site. Cyclodextrins (CDs) have cylindrical structure and have been widely employed as the substrate-recognition moieties in artificial enzymes.[2]

Previously, we reported that α-CD forms complexes with poly(ethylene glycol) (PEG),[3] β-CD with poly(propyleneglycol) (PPG),[4] and γ-CD with poly(methyl vinyl ether) (PMVE)[5] and polyisobutylene.[6] These complexes were formed by the recognition of their main chains. We reported the preparation of a series of copolymers of acrylamide with methacrylates or acrylates with various alkyl chains as guests and the complex formation of these polymers with CDs.[7] These complexes were formed by the recognition of their side chains. CDs were found to bind guest moieties on a polymer chain efficiently and selectively.

– Model Compound –
Acetamide azobenzene (AcAzB)



– Guest Polymer –
Acrylamide–*p*-azobenzene acrylamide (AzBA–AAm) copolymer



– Host Polymer –
Poly(allylamine) with pendant β-CD (β-CD–pAA) copolymer

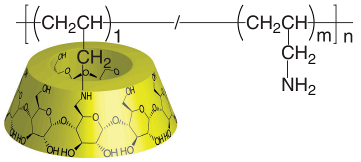
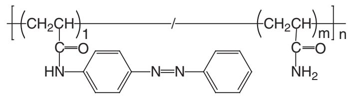


Table 1. Copolymerization of *p*-azobenzene acrylamide (AzBA) and acrylamide (AAm) with AIBN in methanol



Feed mol ratio [AzBA]/[AAm]	Yield/%	Mol ratio[a] [AzBA]/[AAm]	No. of AzBA[a] per polymer	$M_W/10^3$[b]
1/30	24	1/33	2.4	5.5
1/50	22	1/54	1.8	7.0
1/70	36	1/63	4.4	19

[a] Calculated elemental analysis and ^{1}H NMR.
[b] Determined by GPC analysis calibrated with standard poly(acrylamide).

Recently, there are some papers on the cooperative binding of azobenzene in the main chain by CDs[8] and binding of azobenzene on CDs.[9,10] Reversible *trans–cis* (or *E–Z*) isomerization of azobenzenes induced by light has been described in numerous papers.[11] However, to the best our knowledge, there are few papers on the formation of intermolecular complexes of azobenzene attached on a polymer chain. Now, we found guest polymers containing azobenzene groups formed supramolecular gels with host polymers containing β-CD.

The guest polymer was prepared by radical copolymerization of *p*-azobenzene acrylamide (AzBA) and acrylamide (AAm) with AIBN. The AzBA–AAm copolymers were characterized by ^{1}H NMR, SEC, IR and UV–vis. The results of the copolymerization of AzBA and AAm are listed in Table 1. The contents of the azobenzene units were determined by elemental analysis and ^{1}H NMR. After heating the copolymer at 50 °C, the azobenzene groups in a copolymer take *trans* configuration as revealed by UV–vis spectroscopy. The host polymer, poly(allylamine) (pAA) with pendant β-CD side group, was prepared according to the literature.[12] *trans*-*p*-Acetamidoazobenzene (*trans*-AcAzB), a model compound, has been found to bind β-CD with an association constant (K) of 460 M^{-1} in water by UV–vis. *cis*-AcAzB gave the K value of about 2.5 M^{-1}, indicating that the complex formation between azobenzene and β-CD is more favorable for *trans* isomer than for *cis*-isomer. *trans*-AzBA–AAm guest copolymers at mole fraction of AzBA of 1/33, 1/54, and 1/63 have been shown to bind β-CD with association constants of 340, 840, and 750 M^{-1}, respectively. The *cis*-AzBA–AAm guest copolymers, which were obtained by photoisomerization of *trans*-AzBA–AAm with UV light ($\lambda = 360$ nm), were found to have association constants of 10, 17, and 96 M^{-1}, respectively. The results indicate that CDs bind guest moieties of *trans*-azobenzene group on a polymer chain efficiently and selectively.

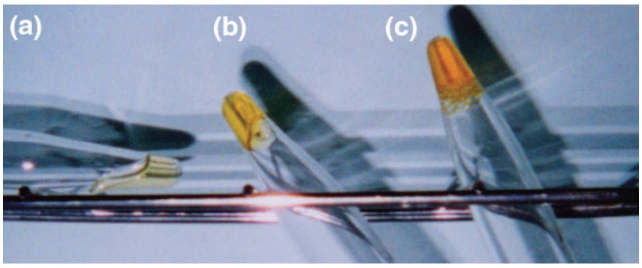


Figure 1. Mixture of AzBA–AAm copolymers and β-CD–pAA copolymers in aqueous solutions at room temperature after 1 day. (a) [AzBA]/[β-CD] = 1/7.7. (b) [AzBA]/[β-CD] = 1/3.8. (c) [AzBA]/[β-CD] = 5.2/1.

On the basis of these results, we investigated the behavior of the mixture of AzBA–AAm guest copolymers (attached on average 4.4 azobenzene molecules on a polymer at run 3 in Table 1) and a β-CD host polymer (attached on average 3.0 β-CD molecules on a polymer). Figure 1 shows a photograph of the mixture of AzBA–AAm copolymers and β-CD–pAA copolymers in an aqueous solution at room temperature after 1 day. The 1:7.7 ratio of [AzBA]:[β-CD] gave a clear liquid with low viscosity (Figure 1a). The viscosity of an aqueous solution was found to increase with increasing AzBA copolymer concentration (Figures 1b and 1c). After a week, all samples lost their fluidity and gave gels. However, *cis*-AzBA–AAm guest copolymers and poly(acrylamide) did not show such gelation with β-CD–pAA host copolymers under any mole ratios. Similarly, *trans*-AzBA–AAm guest copolymers and pAA or β-CD did not show such gelation. β-CD–pAA host copolymers and *trans*–AcAzB did not form gels under any mole ratios. Figure 2 shows proposed structure of the supramolecular gels between *trans*-AzBA–AAm guest copolymers and β-CD–pAA host copolymers.

In conclusion, we prepared copolymers of acrylamide with AzBA and the polyallylamine substituted with β-CD as a host polymer. The association constants between *trans*-azobenzene and the polyallylamine with pendant β-CD were larger than those between *cis*-azobenzene and the polyallylamine with pendant β-CD. We found the polyacrylamide having *trans*-azobenzene formed supramolecular gels with polyallylamine with pendant β-CD. Now, we are studying dynamic aspects of the formation of the supramolecular gels.

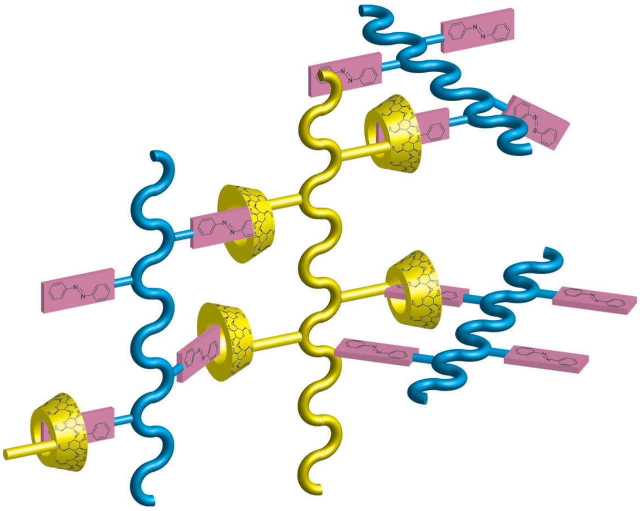


Figure 2. Schematic illustration of supramolecular gels in the mixture of AzBA–AAm copolymers and β-CD–pAA copolymers.

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