Control of the lower critical solution temperature of poly(acrylamide) with azobenzene units

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N-isopropylacrylamides copolymerized with azobenzene-containing acrylamides, which can be dissolved in cold water, are prepared. To increase the solubility of the polymers, we employed toluene containing a small amount of ethanol as a solvent for polymerization to avoid hydrogen bonding of amide units during a chain growth process. The absorption spectra in water showed enlarged and blue shifted n-π* transition bands indicating a strong interaction between water and the nitrogen atom of the azobenzene units. The solutions of the polymer showed changes in lower critical solution temperatures in response to photoirradiation due to isomerization of azobenzene moieties. The photoresponse was observed in the wide range of the introduction amount of the azobenzene unit in the polymer (1-5 mol%). This result differs from the others that were previously reported on similar polymers.
Key words: Azobenzene, N-isopropylacrylamide, LCST

1. INTRODUCTION

Poly(N-isopropylacrylamide) (PNIPAM) undergoes thermal phase transition around 32 °C in water[1]. The temperature is known to be the lower critical solution temperature (LCST): the polymer solution in water is transparent under the LCST, but it becomes turbid above this temperature because of generation of precipitation. This solubility change is due to the coil-globule transition in one polymeric chain, so it is independent of concentration[2]. It is considered that the mechanism includes ordering water molecule structuring and hydrogen bonding. Some applications are proposed using this polymer, such as drug delivery [3] and chromatographic separations[4]. If the polymer responds to other stimulation, it will have a much broader range of applications because thermal stimulation is difficult to access and control in some cases. As one of the examples, a poly(NIPAM) co-polymerized with small amount of photoisomerizable azobenzene units has been already reported to show a photo-induced alternation of transition temperature in a water solution[5]. In such a polymer, it is thought that a polar cis-form of azobenzene can increase solubility for water as compared with a non-polar trans-form because a balance of polar and non-polar moieties is important to control the LCST. In our previous report [6], a polarity dependence of LCST change has been investigated by comparing the calculated dipole moment for different molecular structure of azobenzene moieties. As a result, there was a good relation between photo response of water solubility and their dipole moment change with isomerization.

In this study, we will compare the photoresponses of LCST changes of the solution on irradiation among polymers of substituted azobenzene monomers. The azobenzene monomers have the structure in which azobenzene was attached to polymerizable units via amide bond. Therefore NIPAM and azobenzene monomer have similar structure. We anticipate that the structural similarity will affect interaction not only among polymer segments but also between water and polymer segment.

2. EXPERIMENTALS

2.1 Materials

Chemical structures of azobenzene monomers are shown in Figure 1. These monomers were synthesized from substituted hydroxyazobenzene derivatives via coupling with 1,2-dibromoethane, the replacement of bromide to amine, and amide formation by reaction of amine terminal with acryl chloride. The detailed synthesis will be reported elsewhere [7].

Polymerization: NIPAM and 2, 2'-azobis(isobutyronitrile) (AIBN), purified by recrystallization from ethanol, and azobenzene monomer were dissolved in mixture of toluene and ethanol (4/1 v/v) in the ampoule tube. After the solution was degassed, the tube was sealed and heated for 12 hrs at 60°C with shaking. The viscous solution was poured into ethyl ether for separation of the polymeric materials.

2.2 Physical measurements

Gel permeation chromatography was conducted on Shimadzu system composed of a pump unit LC-10ADvp, a UV-detector SPD-10Avp, a column oven CTO-10Avp and a controller SCL-10Avp. The molecular weight of the polymers was determined using polystyrene standard. LCSTs in water were measured on a Hewlett Packard UV-vis photospectrometer, Agilent 8453, equipped with a thermal controller unit 89090A or Shimadzu

UV-2500PC equipped with a thermal controller, a thermal sensor and a micro-stirrer by monitoring the transmittance of ca. 0.1 wt% of polymer solutions at 700 nm light, where the baseline collection was done using pure water. Irradiation was conducted on an Ushio ultra-high pressure mercury arc through a combination of Kenko color filter Y-43 and Optima QB4 for >400 nm light (vis light) and through a combination of Optima color filters WB360 and ZWB2, for 365nm light (UV light), respectively.
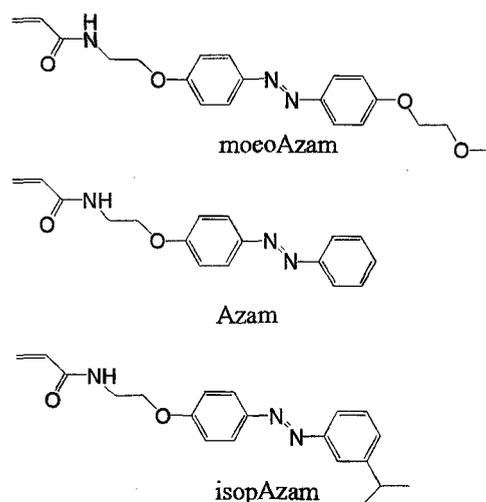

Figure 1. Chemical structures of azobenzene monomers

3. RESULTS AND DISCUSSION
3.1 Polymerization

Copolymerization of NIPAM and isopAzam in benzene has been reported to proceed successfully[6]. On the other hand, polymerization of other az-monomers in benzene or toluene gave insoluble gelled or non-polymeric materials with a high az-content in the feed. The structural difference between isopAzam and the others is the presence of an isopropyl substituent at the lateral position of azobenzene. This structure may decrease the crystallinity and increase the solubility of benzene. We considered that the solubility of the other az-polymers in benzene or toluene was lowered especially with the progress of polymerization due to the symmetrical structure. The polymer separated from the solution during polymerization is likely to form a gel. In this experiment, we employed ethanol-containing toluene as a solvent for polymerization to increase the solubility of the symmetrical az-monomer. Ethanol is an effective solvent for breaking a hydrogen bond, so the addition of ethanol will increase the solubility and promote a chain growth reaction by preventing stacking due to breaking hydrogen bonds between the amide parts in the monomer units. Actually, we obtained soluble polymers in good yield without cross-linking. Molecular weights of all of the polymers were over 10000.

The molar ratios of az-monomer in the feed and the az-unit ratios in the synthesized polymers are listed in Table 1 for each polymerization. The tendency has been seen in which az-unit ratios in the polymers are smaller than those in the feed. We adopted a structure

similar to that of NIPAM; an acrylamide bonded to a saturated hydrocarbon. However, the reactivity is somewhat lower than that of NIPAM. Here, the azobenzene unit contents in the polymers estimated from NMR spectra have a margin of error of ±10 %, due to the much smaller peaks than those of NIPAM and the peak broadening.

Table 1. Copolymerization of NIPAM and Az-monomers

Az-monomers copolymerized with NIPAM	Yield (%)	Az wt% in feed*	Az mol %in feed*	Az mol%in polymer*	Mw ×10⁴	Mw/ Mn
Azam	89.1	1	0.38	0.27	10.4	1.9
	74.4	3	1.14	1.0	10.8	1.7
	92.1	5	1.89	1.5	10.5	1.9
	92.6	7	2.63	2.3	9.7	1.9
	89.1	15	5.47	5.1	7.4	2.7
moeoAzam	99.4	3	0.92	0.74	6.3	1.7
	93.5	7	2.11	1.9	5.5	1.6
	88.2	15	4.42	3.8	3.6	1.8
isopAzam	97.1	3	1.00	0.90	1.8	1.4
	86.0	7	2.30	2.1	2.4	1.7
	74.8	15	4.82	4.1		

*These values represent the ratio of azobenzene units to NIPAM units.

3.2 Photoreaction of azobenzene

Photochemical isomerization of the azobenzene moiety in each monomer was detected by UV-vis absorption spectroscopy. In Figure 2, spectra of poly(moeoAzam/NIPAM) in water are shown as a representative example. Spectra of other az-monomers were similar to those. The spectral features before irradiation corresponded to a thermally stable trans-form. Upon irradiation with 365 nm light, the form changed to a different one with only a small absorption band around 365 nm wavelength, meaning that almost all of the az-monomers isomerized to a cis-form. On irradiation with vis light at 436 nm, ca. 70-80% trans-isomers were generated at a photostationary state.

The spectral shape of trans-form in water is quite different from that in ethanol. The transitions appearing around 400-500 nm and 355 nm are usually attributed to n-π* and π-π* transitions. In water, the π-π* transition was slightly shifted to a longer wavelength, while the n-π* peak was observed as a shoulder of the π-π* peak meaning that the n-π* transition was enlarged and shifted to a short wavelength compared with the ethanol solution. This kind of blue shift is generally seen in azobenzene derivatives because the ground state of an n-π* transition is stabilized in a polar solvent. However, it is difficult to explain such large enhancement of the n-π* transition. At least it is certain that the large blue shift of the n-π* transition band indicates a strong interaction between water and the nitrogen atom of the azo units. A shift and an enhancement of the n-π* transition were also observed in spectra of poly(isopAzam/NIPAM) and poly(Azam /NIPAM) in water, however they are not so much noticeable compared with the poly(moeoAzam-NIPAM) solutions.
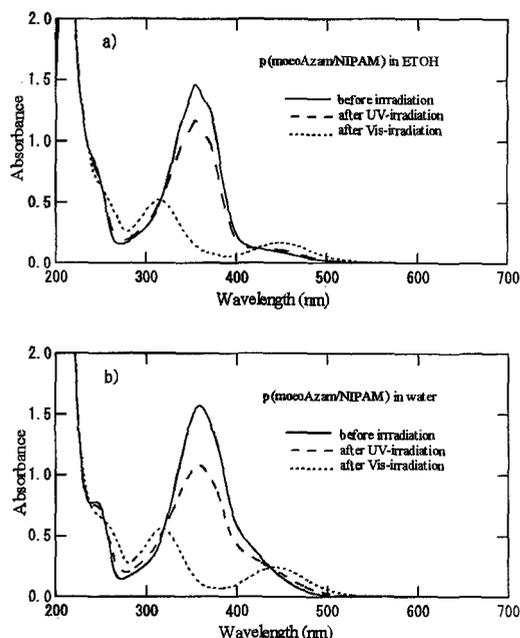
Figure 2.   Absorption spectra of poly(moeoAzam/NIPAM) in a) ethanol and b) water before and after irradiation with UV (365 nm) and vis light (436 nm).

3.3 LCST changes

Poly(Az/NIPAM)s containing azobenzene units except those containing 15 mol% of Az-units were soluble in cold water.   Figure 3 shows temperature dependence of transmittance for the 7wt % of Az-containing polymers in water before and after photoirradiation with UV and vis light.   Regardless of photoirradiation, transmittances in each polymer solution start to decrease at higher temperature owing to light scattering, indicating appearance of polymeric precipitates.   Although some of transmittance values do not reach to zero at high temperature, it is because a transmittance does not reflect solubility of polymer directly.   In other words, if the polymer shrinks tightly, total volume of precipitation should decrease and volume of transparent part should increase in solution. The points at which the transmittance began to decrease were shifted to higher temperature on UV irradiation for all polymers, while vis irradiation induced back shift of that point to lower temperature.   This phenomenon fits the property change with photoisomerization of azobenzene moieties because a cis isomer of azobenzene has a higher polarity than that of a trans isomer.   The values on vis irradiation were close to but slightly higher than the transition temperature before irradiation.   That behavior agrees in the fact that vis irradiation induces cis to trans isomerization with leaving some portion of cis isomer.

The transition temperatures were increased in the order of poly(isopAzam/NIPAM), poly(Azam/NIPAM) and poly(moeoAzam/NIPAM).   It was reflecting properties of substituents such as a hydrophobic isopropyl group, a hydrophilic methoxyethoxyl group and the intermediate between those two in non-substituted azobenzenes.   The sharpness of transition is reduced with increasing hydrophobic property in the

substituent.   The photoinduced LCST shift should depend on total polarity change.   That means that high concentration of azobenzene moieties needed to get large shift of LCST on irradiation.   On the other hand, we have to keep the sharpness of transition.   To dissolve this contradictory problem, hydrophilic substituent will be effective as shown in the transition of poly(moeo-Azam/NIPAM).
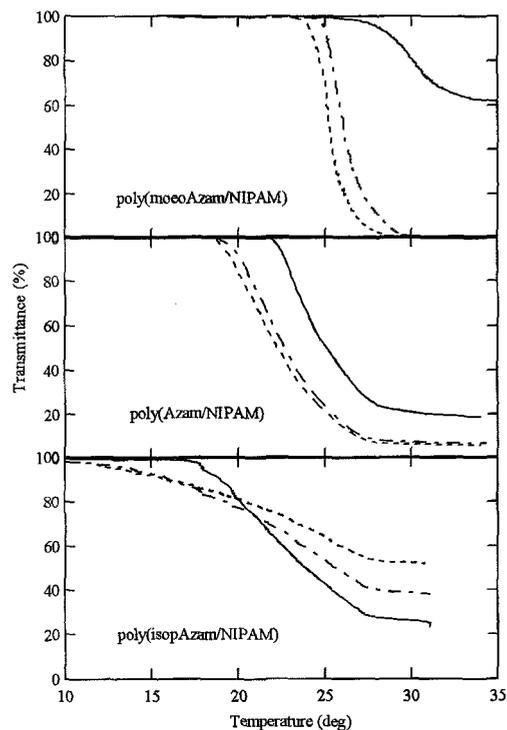

Figure 3.   Transmittance of a) poly(isopAzam/NIPAM), b) poly(Azam/NIPAM) and c) poly(moeoAzam/NIPAM), in a water solution before irradiation (dash line), after UV irradiation (solid line) and after vis irradiation (dotted line) as a function of temperature

In Figure 4, the LCSTs of poly(Azam/NIPAM) on irradiation with UV and vis light are plotted against various az-contents.   The increase in the az-content brought about decrease in the LCST regardless of photoirradiation.   That means that both cis and trans-isomers function as hydrophobic parts or inhibitors to form a water-cluster structure compared with NIPAM units.   At quite low az-content, <1 mol%, there are no temperature differences between UV and vis irradiated samples, indicating that the photoinduced polarity change cannot impart a property change to the entire polymer.   The UV irradiated sample, which contained over 1 mol% azobenzene, consistently showed a higher LCST than that irradiated with vis light.   The temperature difference became a maximum value at around 1.5 mol% of az-content.   Increasing the az-content more than 2 mol% caused a decrease in the temperature difference.   The sample containing over 4 mol % azobenzene was partially insoluble in water. The az-content dependence on the LCST change has already been reported[5], but the az-concentration range showing a photo-induced LCST change was quite narrow in that case.   In our polymer, that point was

improved and become wider because of the increase in solubility of the polymer containing high concentration of az-units.
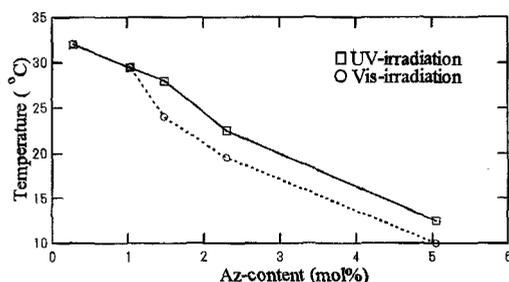

Figure 4. The LCSTs of poly(Azam/NIPAM) on irradiation with UV and vis light are plotted against various az-contents.

4. CONCLUTION

The solubility of our copolymers of NIPAM and azobenzene-containing acrylamides was improved especially in high concentration of azobenzene unit. The polymer showed alternation of the LCST on irradiation with ultraviolet and visible light, which was highly dependent on the structure of the substituent at the azobenzene moieties, especially relating to hydrophobicity.

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