

Photoresponsive Polyacrylamide Based on Grafted Azodianiline

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ABSTRACT: Photoresponsive polyacrylamide (PAA) was synthesized by grafting 4,4'-azodianiline on PAA via the Mannich reaction. The ratio of azo component can be conveniently adjusted through controlling the reaction temperature. Hydrogen bonding between the amino group on the grafted azo component and PAA main chain is utilized to amplify the photoresponse. Dynamic light scatter-

ing study showed that the average hydrodynamic size of PAA having ~ 5 mol % of azo component decreased ~ 24% after UV irradiation at 365 nm. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3244–3248, 2008

Key words: azo polymers; polyamide; graft polymers; photochemistry

INTRODUCTION

Photoresponsive polymers have been widely studied^{1–3} because they are promising in many areas including photooptical media, photo-switches, holographic data storage devices, micropatterning, nonlinear optical media, photomechanical systems, etc.^{4–6} The mechanisms of polymers photoresponse can be classified into three types: (1) trans–cis isomerization of unsaturated bonds in the polymer molecules, (2) reversible photogeneration of strong dipoles in the polymer molecules, and (3) photoinduced ionization of the pendant groups or dopant.^{7,8} In this work, the photoresponse of polyacrylamide are investigated because of the importance of polyacrylamide (PAA) derivatives in both scientific research and industry. PAA has been widely used in drinking water purification, oil recovery, agriculture, biomedical applications, etc.⁹ A photoresponsive PAA may be applied to many of these areas to achieve better control of the processes.

Photoresponse of PAA based on the photoinduced ionization of dopant has been previously reported.^{7,10,11} In this article, we report preparation and characterization of azodianiline modified PAA that showed hydrodynamic size change upon UV light irradiation. Azo compounds have been widely used as photoresponsive materials utilizing its quick trans–cis

conformation change under photoirradiation. Photo-induced deformation and mechanical force generation of azopolymers have been reported.^{5,6,12} Various side-chain and main-chain azocontaining polymers of azopolymers including polyalkenes,^{13,14} polyesters,^{15,16} polyamides,¹⁷ and polyphosphazenes¹⁸ have been studied. In solid state, main-chain azo polymers are expected to have large but slow photoresponse, whereas side-chain azo polymers may result in fast but small photoresponse. To balance the response time and magnitude, we grafted azodianiline on PAA so that the response of the azo side chain can be amplified through H-bonding between the amino group on the azodianiline and the amide group of PAA (Fig. 1). The grafting was achieved through a one-step-modification of commercial available PAA, which is practical and the molecular weight is easy to control.

EXPERIMENTAL

General

All compounds PAA [ACROS, granular, nonionic, average $M_w \sim 6000$], ethylene glycol (ACROS, 99+%), acetone (ACROS, HPLC grade), THF (Fisher, HPLC grade), hydrochloric acid (Fisher, 36.9%), and 4,4'-azodianiline (ACROS, 95%) were used as supplied without further purification. Dynamic light scattering (DLS) measurements of the polymer solution in water were performed with PDDLS/Coolbatch 40T system at 25°C. UV–vis spectra were obtained with Cary 50 scan UV spectrometer at room temperature. Photoirradiation was done by placing the sample ~ 1 cm away from a low-

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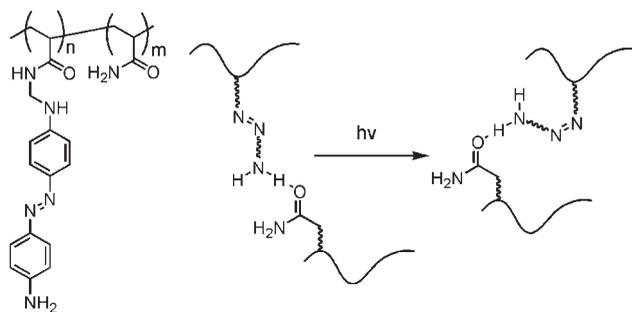


Figure 1 Structure of the synthesized azoPAA and the effect of H-bonding on photoresponse.

intensity Spectroline ENF-280C UV lamp. The intensity is $\sim 1 \text{ mW cm}^{-2}$.

Synthesis of $\sim 0.3 \text{ mol } \%$ PAA

4,4'-Azodianiline (0.3 g, 1.4 mmol) was dissolved into 10 mL ethylene glycol and 0.12 mL formaldehyde solution (ACROS, 37% wt % in water, stab. with 10–15% methanol) was added dropwise and the solution was placed at room temperature for 1 h. The resultant solution was added dropwise into a solution of 0.3 g PAA in 5 mL ethylene glycol. The pH value was adjusted to 5.0 with 1M HCl. Then the mixed solution was kept at 90°C overnight under nitrogen. The mixture was transferred into 500 mL acetone. The precipitate was collected and redissolved into 100 mL ethylene glycol. Excess amount of triethylamine was added to neutralize the product solution. Then the solution was transferred into 500 mL acetone again. These processes were repeated one more time to obtain the light-yellow flocculent solid (40 mg, yield $\sim 13\%$).

Synthesis of $\sim 5 \text{ mol } \%$ azoPAA

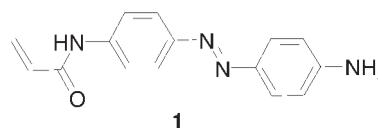
The reaction condition is same as that of the 0.3% polymer except that the reaction maintained over-

night at 120°C under nitrogen. After the reaction, excessive triethylamine was added, and then the mixture was transferred into 200 mL THF. The solvent was evaporated under reduced pressure to $\sim 20 \text{ mL}$. The concentrated solution transferred dropped into 500 mL acetone. The precipitates were filtered off and the acetone solution was concentrated to about 50 mL. The acetone solution was dropped into 1-L water. The blackish precipitate was collected and dried on vacuum at room temperature (65 mg, yield 20%).

RESULTS AND DISCUSSION

Polymer synthesis

In most of the previous works, azogroups containing polymer were prepared by polymerizing azo-containing monomers or copolymerization of azo-containing monomers with other monomer. However, we found that radical polymerization of monomer **1** or copolymerization of **1** and acrylamide



was difficult to achieve. The yield was very low and the molecular weight was hard to control. This may be mostly due to the steric effect of azodianiline. We synthesized azoPAA through the Mannich reaction between commercial PAA and 4,4'-azodianiline with ethylene glycol as a solvent. To get the high conversion ratio, formaldehyde was mixed with 4,4'-azodianiline first to form aldehyde-amine adduct.^{19,20} Then the aldehyde-amine adduct was added into the PAA solution slowly and the pH value of the reaction system was adjusted to 5.0 to start the Mannich reaction (Fig. 2).

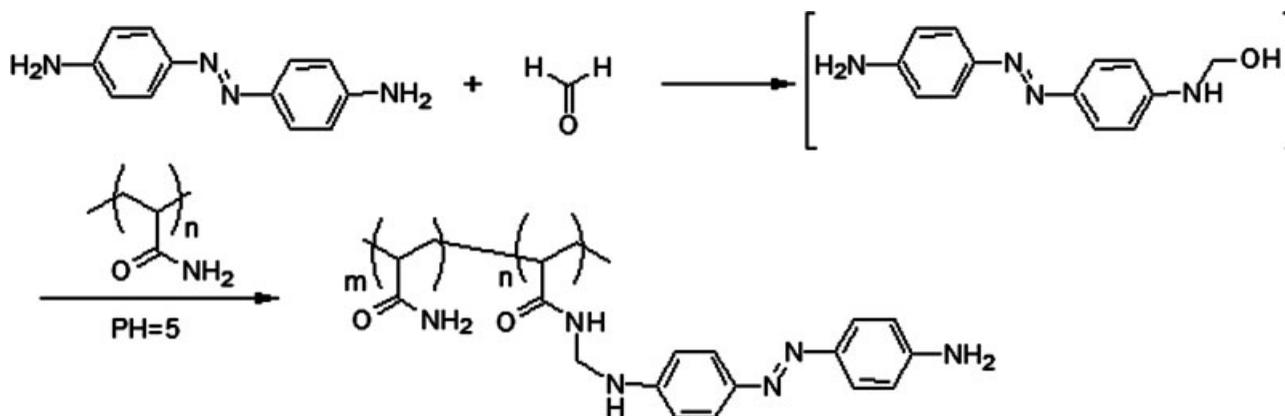


Figure 2 Synthesis of the azodianiline grafted PAA through the Mannich reaction.

Azo-PAA with 0.3 and 5 mol % loading of the azo moieties were synthesized. The loading can be controlled by varying the reaction temperature. Under the condition as described detailed in the Experimental section, reaction at 90°C resulted in only ~ 0.3 mol % loading, whereas ~ 5 mol % loading was achieved at 120°C reaction temperature. The azodaniline could crosslink PAA and result in insoluble products. The 5 mol % polymer collected, characterized, and described in this article is the relatively soluble fractions of the product. Therefore, although higher temperature and concentration may achieve higher loading, the high loading polymers are difficult to characterize due to high crosslinking and low solubility. It is worth mentioning that, given a certain photoresponse, low loading is desired since the properties of PAA can be conserved.

Even though the NMR showed the expected peaks for acrylamide and azodaniline, we cannot determine the loading percentage based on the NMR spectra due to the broadness of the peaks and the low loading, especially for the 0.3 mol % polymer. UV-vis spectra of the polymers were compared with that of 4,4'-azodaniline with known concentration to determine the loading percentage. The UV-vis spectrum of 4,4'-azodaniline in DMSO solution shows a broad absorption above 300 nm, whereas there is no absorption peak of PAA above 300 nm.¹⁸ UV-vis spectra of both polymers showed broad adsorption peaks above 300 nm, which indicated that the azogroups were modified onto the PAA bone (Fig. 5). Therefore, we estimated the concentration of the azo groups through the height of the UV-vis absorption peak at 428 and 393 nm for the higher loading and lower loading polymers correspondingly. We found that the azopolymers synthesized at 90 and 120°C has ~ 0.3 and ~ 5 mol % loading of azo groups correspondingly. The NMR spectrum of ~ 5 mol % polymer showed much stronger peaks in the aromatic region than that of the 0.3 mol % one, which is consistent with the UV-vis spectra data.

Photoresponse of azopolymers

DLS technique was utilized to evaluate the photoresponse of these azogroups modified PAA. The azo PAAs (~ 0.3 and ~ 5 mol %) were dissolved into ultrapure water. The hydrodynamic sizes of these two polymers in water were recorded before and after UV-light irradiation. The DLS experiments indicated that the hydrodynamic size of ~ 5 mol % azo loaded PAA in water is very sensitive to 365 nm UV light. On the contrast, the hydrodynamic size of ~ 0.3 mol % azogroups containing PAA is not sensitive to 365-nm UV light. The hydrodynamic size of 5 mol % azoPAA in water before and after irradiation

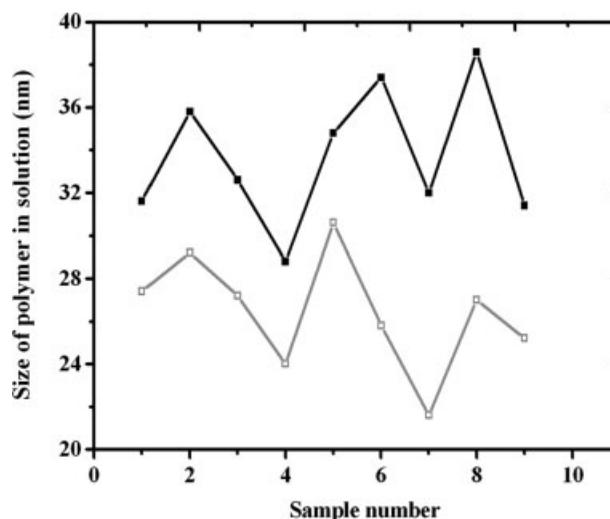
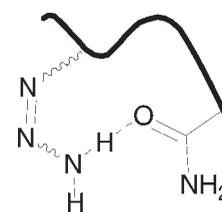


Figure 3 The molecular hydrodynamic size of 5 mol % azogroups containing PAA before (up, filled square) and after (down, hollow square) 60 min of 365nm UV light irradiation (1 mW cm^{-2}) in water.

with 365-nm UV light (intensity $\sim 1 \text{ mW cm}^{-2}$) for 1 h was studied by DLS. Low-intensity UV lamp was used for convenience and following the reaction. Nine different samples were tested to evaluate the photoresponse (Fig. 3). It can be seen that the size changes are consistent. The average hydrodynamic size decreased from 34 to 26 nm, i.e., 24% decrease after irradiation. For ~ 0.3 mol % azogroups modified PAA, there is no obvious hydrodynamic size change when the polymer solution was irradiated with 365-nm UV light for 1 h.

The hydrodynamic size distribution of a ~ 5 mol % PAA before and after 1 h UV light irradiation at 365 nm is shown in Figure 4. The data indicate that the average hydrodynamic size of this sample decreased from 36 to 26 nm. In addition, the distribution of the polymer hydrodynamic size substantially narrowed after the irradiation. The hydrodynamic size distribution was 19.9–125 nm and 19.9–34.4 nm before and after the UV light irradiation correspondingly. The narrowing of the size distribution may result from increase of intramolecular hydrogen bonding due to photo-induced trans-cis isomerization. The



grafted *cis*-azodaniline can form intramolecular hydrogen bond with nearby amide groups, which can lead to a more compact and rigid structure that

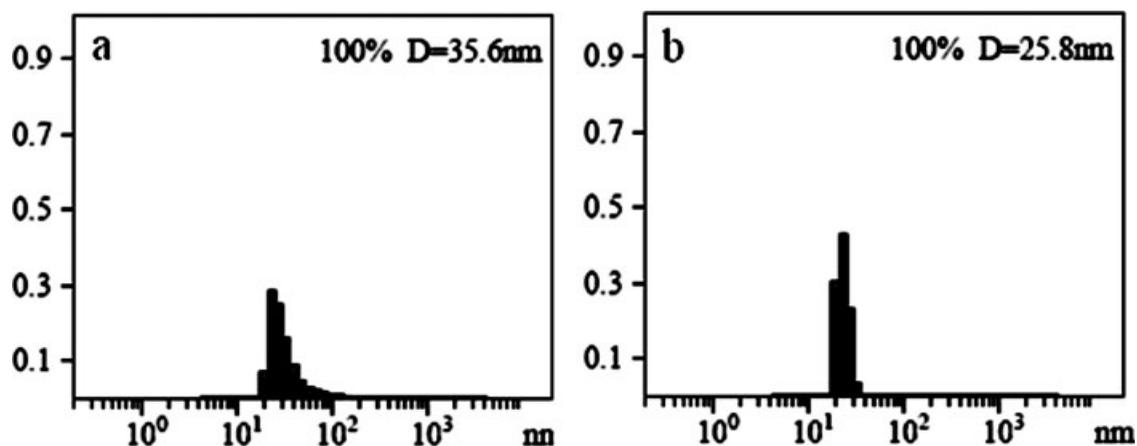


Figure 4 Size distribution of 5 mol % Azo-groups modified PAA in water by DLS measurement. The average hydrodynamic size decreased from 35.6 nm (a, before irradiation) to 25.8 nm (b, after irradiation).

decreases both the hydrodynamic size and distribution. The hydrodynamic size of polymer did not reverse to ~ 34 nm after the sample stayed in dark for 24 h, which shall also be due to the H-bonding that stabilize the *cis*-conformation.

The UV-vis spectra of the azo polymers were also taken in DMSO solution. Figure 5 shows the UV-vis absorbance of the 5 and 0.3 mol % azoPAA, respectively. The low-energy absorption peaked at 428 and 393 nm for 5 and 0.3 mol % azoPAA correspondingly. For 5 mol % azoPAA, after irradiation for 60 min at with 365-nm UV light, the absorption peak blue-shifted about 10 nm and the peak decreased with the irradiation time increased [Fig. 5(a)]. For 0.3 mol % azoPAA, the absorption peak blue-shifted ~ 4 nm and the intensity also decreased [Fig. 5(b)]. The blue shift and intensity

decrease shall result from increased ratio of *cis*-isomer after the irradiation.

CONCLUSIONS

In summary, we have synthesized the azodianiline-grafted polyacrylamide through a one-step Mannich reaction. The azogroups density on the PAA bone can be controlled via the reaction temperature. Our study shows that the hydrodynamic size of 5 mol % azoPAA in water is sensitive to the UV light. Substantial size change ($\sim 24\%$) after photoirradiation was demonstrated. Hydrogen bonding between the amino group of azodianiline and amide group may contribute to the photoresponse. The detailed size change processes and the application of these polymers are under investigation.

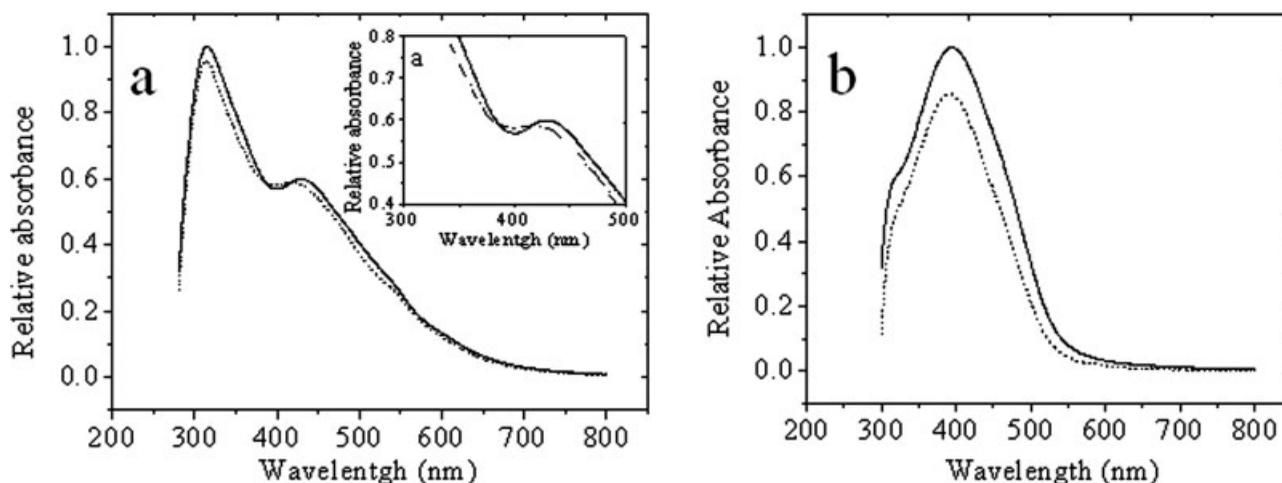


Figure 5 (a) Normalized UV-vis spectra of 5 mol % azogroups modified PAA before (solid line) and after (dash line) 365 nm UV light irradiation for 60 min; the inset is the magnified UV-vis spectra change. (b): UV-vis spectra of ~ 0.3 mol % azogroups modified PAA before (solid line) and after (dash line) 365 nm UV light irradiation for 60 min.

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