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## Hydrogels Self-Assembled from an Azobenzene Building Block: Stability toward UV Irradiation in the Gel and Thin-Film States

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#### Abstract

Azobenzene and its derivatives are widely used as a photoresponsive unit for the fabrication of photoresponsive smart materials. In this work, two kinds of azobenzene derivatives were designed and investigated as hydrogelators, which are N-4-azodiphenyl-maleimic acid (ADPMA) and N-4-azodiphenyl-succinic acid (ADPSA) bearing azobenzene and carboxylic acid segments. In the process of deprotonation/protonation of the carboxylic acids by pH variation, the self-assembly of these two gelators was triggered. ADPMA could transform from solution to hydrogel while the solution of ADPSA formed a precipitate under the same conditions. The solution--gel/precipitate transformation can be repeated by changing the pH. In conventional responsiveness to UV-light irradiation for contrast to the azobenzene-based gels, the ADPMA hydrogel shows typical trans-cis isomerization

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of the azobenzene unit in solution, yet the hydrogel demonstrates remarkable stability to UV light irradiation in both the bulk gel and thin film states.

Stimuli responsive supramolecular materials have attracted more and more attention, because of their applications in diverse areas, like artificial muscle<sup>[1]</sup>, photoswitch<sup>[2]</sup>, biosensors<sup>[3]</sup>, drug delivery<sup>[4]</sup>, and so forth<sup>[5]</sup>. It has been demonstrated that stimuli including temperature, electric field, pH, solvent environment, light and anions/cations<sup>[6]</sup> could trigger the dramatic variation of material properties, assisting the fabrication of smart materials. Compared with the other stimuli, light can be easily switched on and off, noninvasive, controlled remotely and precisely, and can lead to a fast response<sup>[7]</sup>. Thus, light as a stimulus has been aggressively pursued by chemists and materials scientists. Photoresponsive chromophores, such as butadiene<sup>[8]</sup>, dithienylethene<sup>[9]</sup>, spiropyran<sup>[10]</sup>, azobenzene<sup>[11]</sup>, stilbene<sup>[12]</sup> and anthracene<sup>[13]</sup> groups, are widely introduced to from photo-responsive materials.

Azobenzene and its derivatives are capable of changing from a more stable trans configuration to a less stable cis configuration under UV light irradiation, of which process is reversible. The change of configuration after UV light irradiation always result in the change of systems' properties, such as gel–sol transitions<sup>[14]</sup>, binding and releasing guest molecules<sup>[15]</sup>, association–dissociation of aggregates<sup>[16]</sup>, deformation of colloidal particles<sup>[17]</sup> and changing of morphology<sup>[18]</sup>. Moreover, azobenzene unit is widely used to fabricate  $\pi$ -conjugated systems<sup>[19]</sup>. The  $\pi$ -conjugated systems could accept or donate electrons easily, have low energy excitations in the visible spectral

region and could absorb visible light<sup>[20]</sup>. Given the above, azobenzene and its derivatives have fantastic applications in optics and electricity<sup>[21]</sup>. Nevertheless, due to the extremely sensitivity to UV light, in some special cases such as pigments or painting, it limits the application of azobenzene moieties.

To this end, we designed two kinds of molecules containing azobenzene unit and carboxylic group (Scheme 1). Azobenzene group was introduced as photoresponsive And carboxylic/carboxylate group moiety. shall switch reversibly upon deprotonation/protonation, that caused the molecular responsive to pH<sup>[22]</sup>. Amide group could undergo keto-enol tautomerization<sup>[23]</sup>, where enol configuration conjugated with -C=C- and azobenzene unit form  $\pi$ -conjugated system in N-4-azodiphenyl-maleimic acid (ADPMA). However, N-4-azodiphenyl-succinic acid (ADPSA) without -C=C- could not form  $\pi$ -conjugated system (Scheme 1). We studied their self-assembly in aqueous with different pH, respectively. ADPMA formed hydrogel by changing pH, while ADPSA precipitated. We further investigated the photo-responsive property of ADPMA. The solution of ADPMA is photoresponsive, but the hydrogel which formed by adding acid is UV-irradiation stable. The hydrogel transformed into solution again with the adding of base, and the property of photo-responsive recovered. It is believed that the relative tight molecular stack between azobenzene moieties contribute greatly to the emergence of UV stability. It is an effective strategy to avoid the light responsive property for azobenzene unit as needed.



Scheme 1. Schematic representation for chemical structures of ADPMA, ADPSA, and self-assembly behaviors of ADPMA.

Change of pH is a simple and effective chemical method to form gel. The process of self-assembly largely relies on reversible protonation/deprotonation of carboxyl/carboxylate. The phase transition process of ADPMA that triggered by the addition of acids and bases has been shown in Figure 1. ADPMA has poor solubility in water (Figure 1a) while in basic environments it can be well dissolved. A transparent solution was obtained by adjusting pH to around 7-8 (Figure 1b). The transparent solution was transformed to the hydrogel after adding acid (Figure 1c). And the hydrogel could be transformed into solution again instead of returning back to precipitate with the addition of base (Figure 1d). The phase transition process of ADPMA also could be triggered by other alkalis and acids (Figure S3). However, N-4-azodiphenyl-succinic acid (ADPSA) did not transform into hydrogel. Instead, precipitate was attained under the same situation and the transformation of solution to precipitate was revisable, as well (Figure S4). Variation of the parameters (such as, concentration of acid/base, kind of acid/base and the concentration of ADPSA), only the transformation from solution to precipitate was discovered. ADPMA and ADPSA

displayed various transformations by changing pH. Comparing the structures of ADPMA and ADPSA, the ADPMA could form a  $\pi$ -conjugated system (Scheme 1), which shall strengthen the intermolecular interactions of ADPMA in water. Because of the reversible deprotonation/protonation of carboxyl/carboxylate, it resulted in a significant change of ADPMA solubility in water, and the gel formed by changing pH is reversible.



**Figure 1.** Photographs of phase transition process of the system from (a) ADPMA in neutral water ( $C_{ADPMA} = 0.4$  wt %), (b) transparent solution by adding NaOH ( $V_{NaOH} = 68 \ \mu L$ ,  $C_{NaOH} = 0.5 \ mol/L$ ), (c) hydrogel by injecting HCl ( $V_{HCl} = 68 \ \mu L$ ,  $C_{HCl} = 1 \ mol/L$ ), (d) solution by adding NaOH ( $V_{NaOH} = 136 \ \mu L$ ,  $C_{NaOH} = 0.5 \ mol/L$ ).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the morphology of self-assemblies of ADPMA in different conditions. In alkaline solution, irregular particles and fibers co-existed (Figure 2a-c). In enlarged images, it can observe that the irregular particles were actually formed by nanoscale fibers. The self-assembly of ADPMP is relatively disorder in alkaline solution. By adjusting pH, the solution was triggered into the hydrogel. In contrast, only fibers were probed with widths ranging from 100 to 300 nm (Figure 2d-f). Decreasing pH further, the gelation period is shortened. And the fibers of hydrogel became thinner. Only fibers were observed with different diameters in hydrogels that triggered by different kinds of bases and acids (Figure S5). The addition of acid

increased the strength of non-covalent forces, which favors transformation of gelator from disordered self-assembly to ordered fibers. Repeating this process of sol-gel for up to five times, hydrogel also formed and the diameter of fiber almost unchanged (Figure 2g-h).



**Figure 2.** (a-b) TEM images of ADMPA ( $C_{ADPMA} = 0.4$  wt %) in alkaline solution ( $C_{NaOH} = 0.5$  mol/L,  $V_{NaOH} = 68$   $\mu$ L). (c) SEM image of ADMPA in alkaline aolution. (d-e) TEM images of hydrogel formed by adding acid ( $C_{HCI} = 1 \text{ mol/L}$ ,  $V_{HCI} = 68 \mu$ L). (f) SEM image of hydrogel. (g-h) TEM image of hydrogel after repeating solution-gel process for five times. (i) SEM images of hydrogel after repeating solution-gel process for five times.

Rheological characterization was conducted to study the rigidity and flow behavior of the hydrogel. Dynamic oscillatory stress sweep and frequency sweep of the gel are shown in Figure 3a, b. The strain response to an applied stress can be described as two dynamic moduli (the elastic modulus G' and the viscous modulus G''). The elastic modulus G' (solid-like behavior) is a quantity that measures materials' resistance to being deformed elastically. The viscous modulus G'' (liquid-like behavior) estimates the flow ability of materials against external stress. G' values are higher than that of G'' in the linear viscoelastic region, implying the gel display an elastic behavior

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(solid-like behavior). When the high oscillatory stress over 163.7 Pa, the elastic modulus G' and the viscous modulus G" both show sharp decrease and the solid-like gel begins to flow. The dynamic frequency sweep measurement results are shown in Figure 3b. Within the measurement frequency range, the G' is always much higher than G". Both G' and G" values of the hydrogel are slightly frequency-dependent, which means some weak matrixes exist in the gel. In addition, the magnitude of G' is relatively high which proves good mechanical strength of the hydrogel.



Figure 3. (a) Dynamic oscillatory stress sweep of the hydrogel. (b) Frequency sweep of the hydrogel. (c) FT-IR spectra of ADPMA and xerogel. (d) SWAXS of hydrogel ( $C_{ADMPA} = 0.4$  wt %,  $\lambda = 365$ nm, t = 2 h).

Fourier transform infrared spectroscopy (FT-IR) is widely used to provide information about hydrogen bonding. Figure 3c shows the spectra of ADPMA and the xerogel, illustrating the essential characteristic IR peaks for special hydrogen bonds. The stretching vibration of the carbonyl in -COOH emerges at 1701 cm<sup>-1</sup>, and amide I band (the stretching vibration of the carbonyl in amide groups) presents at 1630 cm<sup>-1</sup> while amide II bands (the N-H bending mode and the stretching vibration of C-N in amide groups) exist at 1556 cm<sup>-1</sup> in ADPMA. These characteristic peaks appeared suggesting the presence of intermolecular H-bonding. And the position of amide Π exhibits a large shift to lower wavenumber (1544 cm<sup>-1</sup>) in xerogel, suggesting that H-bonding interactions between the amide groups were strengthened in hydrogel.

The small- and wide angle X-ray scattering (SWAXS) patterns<sup>[24]</sup> of the gel were used to provide essential evidence of the molecular arrangement in the well-defined aggregates, as shown in Figure 3d. The hydrogel of ADPMA was further analyzed. The extended length of one ADPMA molecule was about 1.65 nm, as estimated from the optimized molecular modeling based on Material Studio 5.0 software. The first intense scattering peak at 5.72 nm<sup>-1</sup> corresponds to a d-spacing of 1.1 nm (d =  $2\pi/q$ ) smaller than the extended length of one ADPMA, may be because the molecule of ADPMA bended in hydrogel assembly. The three major peaks at scattering vectors (q) of 5.72 nm<sup>-1</sup>, 11.48 nm<sup>-1</sup>, and 17.36 nm<sup>-1</sup> are quite close to the ratio of 1:2:3. Thus the data are consistent with the present of a well-defined lamellar structure. In addition, the broad scattering peak at 14.83 corresponds to a d-spacing of 0.42 nm is likely to shows the distance between two molecules perpendicular to lamellar orientation (Scheme 1) of the hydrogel.

The azobenzene unit would fast change from a more stable trans configuration to the less stable cis configuration under UV light irradiation ( $\lambda = 365$  nm), possibly leading to the gels containing azobenzene groups undergo gel-solution changes with short periods of UV light irradiation. On top of this, we studied the photo-responsive property of the hydrogel formed by changing pH. However, the hydrogel showed neither this gel-solution transformation nor other obvious changes, even if the UV light irradiation lasts for two days (Figure 4a). It is predicted that the unusual hydrogel may stable to UV light irradiation. TEM and SEM were used to further investigate the morphological changes of hydrogel with UV light irradiation. Fibers were detected with diameters 100-300 nm (Figure 4b, c), which consistent with the hydrogel without UV light irradiation (Figure 2b, d). TEM and SEM images suggested the morphology of hydrogel is stable after UV light irradiation. Both macroscopic and microscopic morphology did not change after UV light irradiation, indicating the UV light irradiation stability of hydrogel.



**Figure 4.** (a) Pictures of hydrogel after UV-irradiation ( $\lambda = 365$ nm) with different times. (b) TEM image of hydrogel after UV-irradiation ( $\lambda = 365$ nm, t = 1 h). (c) SEM image of hydrogel after UV-irradiation ( $\lambda = 365$ nm, t = 1 h). (d) UV-vis spectra of ADPMA in alkaline solution (CADPMA = 4×10-3 wt %,  $\lambda = 365$ nm, t =3 min). (e) UV-vis spectra of hydrogel (C<sub>ADPMA</sub> = 0.4 wt %) upon UV light irradiation ( $\lambda = 365$ nm, t =1 h)

UV-Vis was employed to study the changes of solution and hydrogel upon UV light irradiation. Expectedly, the solution of ADPMA shows typical UV light-induced trans-cis isomerization property of azobenzene group (Figure 4d, S6). The peak at 356 nm was attributed to the  $\pi$ - $\pi$ \* transfer of the azobenzene trans-isomer, whereas the  $n-\pi^*$  transfer of the cis-isomer was at 436 nm. The intensity of the  $\pi-\pi^*$  transfer peak gradually decreased and the position of the peak became blue shifts. At the same time, the intensity of the n- $\pi^*$  transfer peak gradually increased. The equilibrium state was basically reached after 3 min of irradiation, indicating that the cis and trans isomers of azobenzene group almost reached equilibrium at this time. However, the peak position of hydrogel did not occur obvious shift (Figure 4e) after sufficient UV light irradiation, which suggesting the UV light irradiation has limited impact on the hydrogel. The solution and hydrogel transformation is controlled by the addition of acid and base. It is an effective strategy to avoid the light responsive property of azobenzene unit under special circumstances, which may extend the application of azobenzene derivatives in the field of functional material.

Moreover, the SWAXS was used to further identify the hydrogel's property of UV light irradiation stability and study the molecular arrangement of the hydrogel after UV light irradiation. As shown in Figure 3d, the position of peaks and relative peak intensities of hydrogel after UV light irradiation were identical with the hydrogel before UV light irradiation, which indicating the molecular arrangement of the hydrogel upon UV light irradiation has not been altered. It is commonly believed that the trans-cis isomerization of azobenzene may proceed via a rotation about the N=N bond, or via inversion of one of the nitrogen atoms<sup>[25]</sup>. The amide group of molecule could undergo a keto-enol tautomerization which forming a  $\pi$ -conjugated system. And Accepted Manuscript

the molecular arrangement of the hydrogel is tight and ordered, which also confined the occurring of trans-cis isomerization. Thus, the hydrogel has the properties of UV-irradiation stability.

In summary, the two kinds of azobenzene derivatives (ADPMA and ADPSA) displayed different phase transformation via pH variation. ADPMA transformed into hydrogel by changing pH, while ADPSA turned to precipitate. ADPMA simultaneously self-assembled into irregular particles constituted by ultra thin fibers in alkaline solution, with relatively disordered molecular arrangement. After adding acid, the solution of ADPMA was transformed into hydrogel with entangled thin fibers. The molecular arrangement of hydrogel exhibits well-defined lamellar structure. The different ways of self-assembly could be controlled reversibly by changing pH. Moreover, ADPMA shows typical photoresponsive property in alkali solution, yet the hydrogel which formed by ADPMA is UV light irradiation stable even under long time light irradiation. It is a potential strategy to avoid photoresponsive properties of azobenzene unit for special material fabrication.

#### **Experimental Section**

4-aminoazobenzene and maleic anhydride were purchased from Aladdin Bio-chem Technology Co. Ltd, Shanghai, China. All other reagents were obtained from commercial sources and used without further purification.

N-4-azodiphenyl-maleimic acid (ADPMA) and N-4-azodiphenyl-succinic acid (ADPSA) were prepared according to the reported literatures <sup>[26]</sup>. In detail, 4-Aminoazobenzene (1.97 g, 10 mmol) and maleic anhydride (1.18 g, 12 mmol) were dissolved in acetone

respectively. The solution of maleic anhydride was added drop-wise to a cooled solution of 4-Aminoazobenzene at 0-5°C and the mixture was stirred for 6 h at 0-5°C. The orange solids of ADPMA were filtered and washed with acetone for several times. The wet filter cake was dried at 55°C for 48 h under vacuum drying oven. ADPMA was purified by recrystallization from methanol. 1 H NMR (400 MHz, DMSO)  $\delta$  12.96 (s, 1H), 10.68 (s, 1H), 7.93 – 7.85 (m, 6H), 7.61 – 7.52 (m, 3H), 6.52 (d, J = 12 Hz, 1H), 6.35 (d, J = 12 Hz, 1H)

4-Aminoazobenzene (1.97 g, 10 mmol) and succinic anhydride (1.20 g, 12 mmol) were dissolved into 25 ml acetone. Anhydrous pyridine (0.79 g, 10 mmol) was added into the solution and the mixture was stirred for 6 h at 60°C. The obtained suspension was filtered, washed and dried at 55 °C. 1 H NMR (400 MHz, DMSO)  $\delta$  12.15 (s, 1H), 10.33 (s, 1H), 7.89 – 7.81 (m, 6H), 7.61 – 7.51 (m, 3H), 2.63 (t, J = 8 Hz, 2H), 2.55 (t, J = 8 Hz, 2H).

ADPMA was weighed 10 mg into a test tube. Deionized water (2.5 mL) was added. This solution was then sonicated for 5 minutes. NaOH (68  $\mu$ L, 0.5 M) was slowly added and sonicated to aid ADPMA dissolving, until a clear solution was obtained. HCl (68  $\mu$ L, 1 M) was added into the clear solution as quickly as possible. Let it maintain for a while, and the hydrogel was formed. ADPMA can self-assemble into hydrogels with different kinds of bases and acids by similar process as mentioned above.

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were obtained on a Bruker Advance DMX 400 MHz instrument at room temperature. Internal standard is tetramethylsilane (TMS) and solvent is DMSO. Transmission electron microscope (TEM) images were measured on a JEM-100CX electron microscope. The samples for TEM detection were dropped in the copper wire mesh and dried under the infrared lamp. Scanning electron microscope (SEM) pictures were gotten with a HitachiS-4800 scanning electron microscope. The samples for SEM detection were dropped in the silicon pellet, dried and then sprayed by the gold. FI-IR spectrums were obtained by an Avatar 370 FT-IR Spectrometer with KBr pellet method at room temperature. The xerogel of ADPMA was obtained by vacuum drying of the hydrogels for 12 h until become dried powders at 30°C. UV-vis curves were gotten at room temperature with a TU-1800pc. Rheological properties were measured by a Thermo HaakeRS300 rheometer. The frequency spectra were conducted in the linear viscoelastic regime of the samples determined from dynamic strain sweep measurements at 25°C. Small and wide angle X-ray scattering (SWAXS) date were collected at room temperature with SAXSess mc2 from Anton Paar. The apparatus was operated at 40 kV and 50 mA using Cu Ka X-rays (wavelength of 0.154 nm). The X-ray irradiation time was fixed at 30 min.

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**Keywords:** azobenzene derivatives • isomerization •  $\pi$ -conjugated systems • photoresponsive materials • supramolecular hydrogels

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In ADPMA, amide group could undergo keto-enol tautomerization, where enol configuration conjugated with -C=C- and azobenzene unit form  $\pi$ -conjugated system. ADPMA could transform from solution to hydrogel while the solution of ADPSA formed a precipitate under the same conditions. The ADPMA hydrogel shows typical trans-cis isomerization of the azobenzene unit in solution, yet the hydrogel demonstrates remarkable stability to UV light irradiation in both the bulk gel and thin film states.