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Solvothermal Synthesis of a New Photochromic Azo Polymer and its Self-assembly Behavior

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An amphiphilic azobenzene diblock copolymer {2-[4-(4-methoxy phenyl azo)phenoxy]hexyl acrylate co-acrylic acid} was synthesized via reversible addition-fragmentation chain transfer polymerization in a hydrothermal reactor. The products were characterized by ^{1}H-NMR, DSC, GPC and UV-Vis spectroscopy. Different self-assembly behaviors of this amphiphilic diblock copolymer in different organic solvent with different water content were investigated. In THF/H_2O solution, the diblock copolymer self-assembled into spheres and the spheres would then change to vesicles with smaller size by increasing the volume of H_2O. However, in DMSO/H_2O solution, the sizes and morphologies of the self-assembled spheres would not change significantly with an enhanced amount of H_2O. Photochromic behaviors of the amphiphilic diblock copolymer in different enviorments were investigated. The photoisomerization rate of PAzoM-b-PAA in the film is much lower ($k = 6.058 \times 10^{-3} s^{-1}$) than that in the THF/$H_2O$ suspension ($k = 1.107 \times 10^{-2} s^{-1}$). A rotational mechanism was suggested for the isomerization process of PAzoM-b-PAA.

Keywords: Self-assembly, azobenzene, copolymer, photoisomerization

1 Introduction

In recent years, intense investigations have been devoted to azobenzene-containing polymers (azo polymers for short) because of their potential applications in the fields of optical data storage, liquid crystal displays, and holographic surface relief gratings (1–5). The fascinating photoresponsive variations of azo polymers such as phase transition, chromophore orientation, surface-relief-grating formation, and photomechanical bending are based on the trans-to-cis and the cis-to-trans photoisomerization of azobenzenes, which lead to considerable changes in their molecular shape and dipole moments (6,7). It has been proved that the photoresponsive properties of azo polymers depend on the molecular architecture such as chemical structure of backbone, types of azo chromophores, and positions to which azo chromophores are attached. Molecular design and synthesis of azo polymers with different photoresponsive properties become crucial in the investigation of azo polymers.

Colloidal particles, which have at least one dimension within the nanometer to micrometer range, have been used in many industrial products such as inks, paints, coatings, cosmetics, and photographic films (8). Recent studies have expanded the applications of polymer-based colloids to new areas such as microreactors, targeted drug delivery, and mimic for biological membranes (9,10). Amphiphilic block copolymers can self-assemble to form micellar aggregates of various morphologies including star micelles, crew-cut micelles, rods, and vesicles with narrow size distribution in selective solvents (11,12), and they have been proved to have advantages in drug delivery and diagnostic systems (13). Self-assembled colloidal particles composed of amphiphilic azo polymers can combine interesting properties of azo polymers and colloidal particles. The cooperative properties, as well as some amazing derivative ones, will be exhibited in the self-assembled system.

Solvothermal synthesis is considered to be a soft chemical route with important advantages in inorganic chemistry and it can directly provide production without any firing step. This method requires neither sophisticated processing nor high interaction temperature, and it is essentially less energy intensive, less polluting and leads to high homogeneity products. The interaction is carried out in Teflon-lined stainless steel autoclaves, which can automatically generate high pressure in the process. Due to the above advantages, we first applied the inorganic Solvothermal synthesis method to the polymerization

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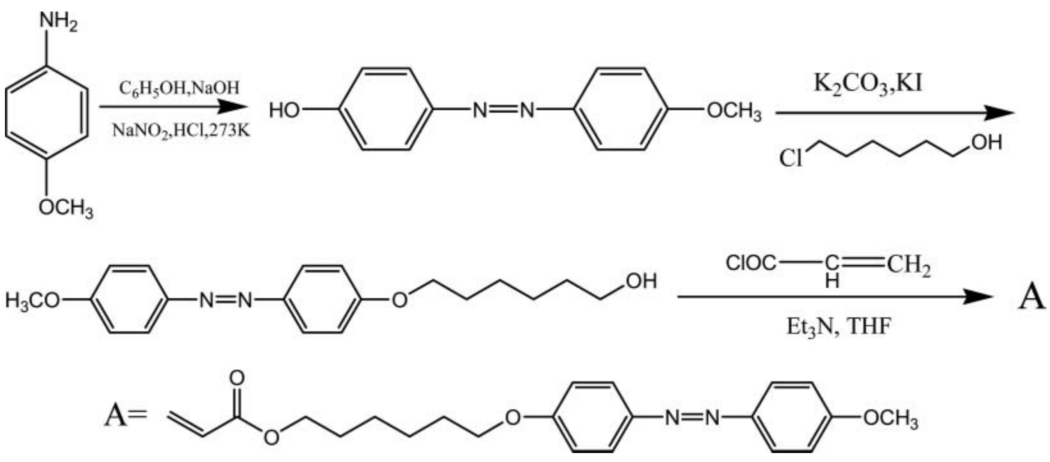


Sch. 1. Synthetic route of 2-[4-(4-methoxy phenyl azo)phenoxy]hexyl acrylate.

of the copolymers. In the present work, we reported the synthesis of an azo diblock copolymer {2-[4-(4-methylphenylazo)phenoxy]hexyl acrylate co-acrylic acid} (PAzoM-b-PAA) via reversible addition-fragmentation chain transfer (RAFT) polymerization. To realize the anhydrous, high-pressure, and nitrogen environment, we first utilized hydrothermal reactor to process the polymerization. Many factors, such as the degree of functionalization, water content in the solvent mixture, nature and composition of the solvent, provide control over the self-assembly behaviors of amphiphilic azo polymers. X. Wang et al. (14) have reported the effect of the degree of functionalization on the formation of the colloidal spheres. So, in our paper, we put our efforts on the effects of different solvents on the formation of the colloidal spheres. The self-assembly behaviors of PAzoM-b-PAA in THF/H_2O solution and seldom reported DMSO/H_2O solution with different water concentration were investigated, respectively. In addition, the photochromism of azo polymer in the film and in the THF/H_2O suspension were also discussed.

2 Experimental

2.1 Materials

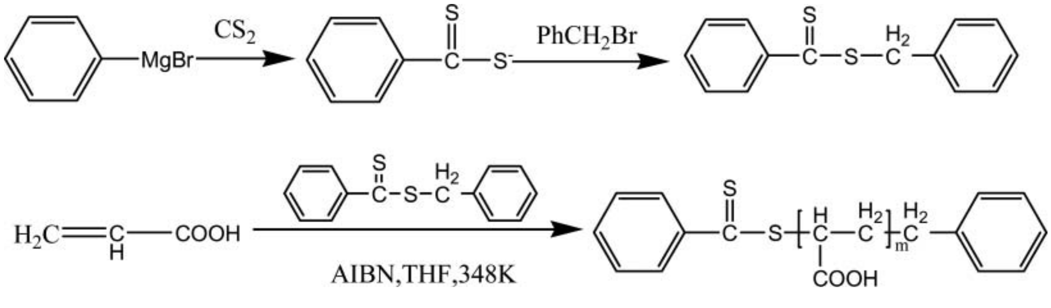
Acryloyl chloride was purchased from Alfa Aesar. 2,2′-azobisisobutyronitrile (AIBN), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and hexachlorohexanol were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were of analytical grade. All the solvents were freshly distilled and DMF was dehydrated before use.

2.2 Preparation of 2-[4-(4-Methoxy phenyl azo)phenoxy] hexyl Acrylate (AzoM)

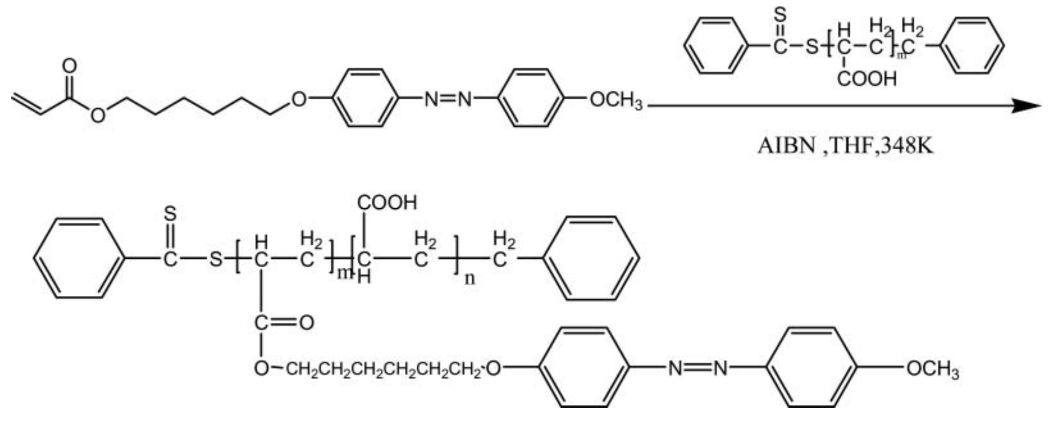
The synthetic route of the monomer AzoM was illustrated in Scheme 1 according to the procedure similar to the published method (15). The purity of the monomer was guaranteed by elemental analysis.

2.3 Preparation of the Addition-Fragmentation Chain Transfer Agent

The synthetic route of the addition-fragmentation chain transfer agent dithiobenzoate [S=C(Ph)S–Ph] was illustrated in Scheme 2, according to the literature (16). Acrylic acid (1 g), [S=C(Ph)S–Ph] (0.02 g), AIBN (0.25 mg) were dissolved in anhydrous THF (2 mL). After stirring with a magnetic stirrer for 30 min, the reaction mixtures were then transferred to Teflon-lined stainless steel autoclaves with N_2 protection for 10 min to eliminate O_2. The autoclaves were then put in a common oven and heated at 75°C for 20 h. The whole polymerization was carried out under



Sch. 2. Synthetic route of the addition-fragmentation chain transfer agent dithiobenzoate [S=C(Ph)S–Ph].



Sch. 3. Synthetic route of the PAzoM-b-PAA diblock copolymer.

autogenous pressure with N_2 protection and sealed environment. The product (PAA-SCS(Ph)) was recovered by precipitating into excess of ether. The reprecipitation procedure was carried out three times. The product was dried in a vacuum oven at 40°C for 24 h.

2.4 Preparation of the Block Copolymer and its Film

The synthetic route of PAzoM-b-PAA diblock copolymer was outlined in Scheme 3. PAA-SCS(Ph) (0.165 g), AzoM (0.245 g) and AIBN (0.5 mg) were dissolved in anhydrous THF (5 mL). The mixture was then transferred to the Teflon-lined reactor with N_2 protection, and was heated at 75°C for 20 h (similar to the process described in section 2.3). The polymer was obtained by precipitation in ether. It was purified three times and dried in a vacuum oven. The film of the polymer was obtained by dip-coating from THF solution (10 wt%) onto a quartz surface.

2.5 Preparation of PAzoM-b-PAA Colloidal Spheres and Vesicles in Different Solvents

The self-assembly process was performed by adding Milli-Q water at a rate of $10\mu L/s$, with stirring, into a THF solution of the diblock copolymer with the initial concentration of 5 mg/mL. Samples in mixed THF/H_2O solvents with different water concentration of 60 vol%, 70 vol%, 80 vol% and 90 vol% were obtained.

The preparation of PAzoM-b-PAA colloidal spheres in $DMSO/H_2O$ solution was similar to that in THF/H_2O solution. Samples in mixed $DMSO/H_2O$ solvents with different water concentration of 60 vol% and 90 vol% were obtained.

2.6 Measurements

The ^{1}H-NMR spectra of the block copolymer was measured in $CDCl_3$ using a UNITY INOVA 600 NMR spectrometer. Thermal phase transitions were examined using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C/min. An Agilent 1100 series gel permeation chromatography (GPC) system equipped with a LC pump, a PLgel 5 μm Mixed-C column calibrated using linear polystyrene standards and a refractive index (RI) detector was used to determine polymer molecular weights and molecular weight distributions. UV-Vis spectra were recorded on a SHIMADZU UV-2300PC spectrophotometer. Colloidal spheres and vesicles were observed using a JEM-100SX transmission electron microscope (TEM) and a Tecnai/G2 20S-TWIN Philip transmission electron microscope.

3 Results and Discussion

3.1 Characterization of Polymers

The molecular weights (M_n) of the macroinitiator PAA-SCS(Ph) and the diblock copolymer PAzoM-b-PAA were determined by GPC. The results are as follows: M_n(PAA-SCS(Ph)) $= 2.16 \times 10^4$, M_w/M_n(PAA-SCS(Ph)) $= 1.10$, M_n(PAzoM-*b*-PAA) $= 3.18 \times 10^4$, and M_w/M_n (PAzoM-*b*-PAA) $=1.06$. By calculation, the ratio of the two segments was 26(PAzoM)/296(PAA). It is clear that the growth of the PAzoM block from the macroinitiator proceeds in a controlled way.

The DSC heating curve of the diblock copolymer PAzoM-*b*-PAA is shown in Figure 1. PAzoMA is known to have a smectic (S) and nematic (N) phase (17, 18). The glass transition was observed to occur at $Tg = 79$ °C, the liquid crystalline transition at 99°C, and the isotropic transition at 128°C.

The composition of the block copolymer PAzoM-*b*-PAA is determined by ^{1}H-NMR spectrum, which is illustrated in Figure 2.

3.2 Self-assembly of PAzoM-b-PAA in Different Solvents

Amphiphilic polymers can self-assemble into ordered architectures such as spheres, rods, lamellae, and vesicles in suitable solvents. THF and DMSO are used to dissolve both

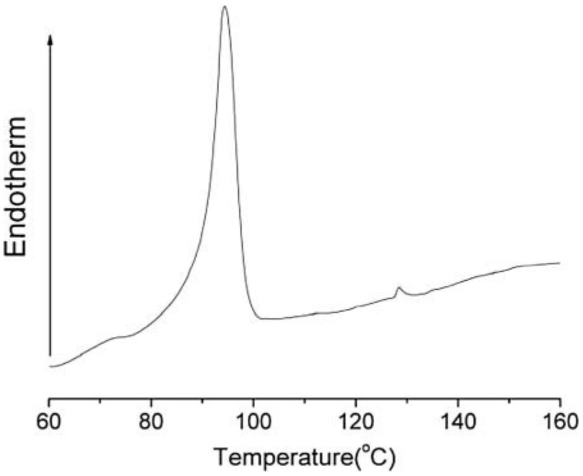


Fig. 1. DSC heating curve of PAzoM-*b*-PAA.

the hydrophobic and hydrophilic blocks of PAzoM-*b*-PAA to form a diblock copolymer solution, respectively. Water is added as a precipitant for the hydrophobic block to induce self-assembly. Colloidal spheres are obtained through gradual hydrophobic aggregation of the polymeric chains in THF/H_2O and DMSO/H_2O dispersion media, which is induced by continuous increase of the water content in the media. Generally, the formation of block copolymer aggregates of various morphologies is controlled by a force balance between three different factors: the degree of stretching of the core-forming blocks, the interfacial tension between the micelle core and the solvent outside the core, and the repulsive interactions among corona forming chains (19). In solution, many factors, such as different copolymer composition, the temperature, the nature of the common solvent, the amount of water present in the solvent mixture etc. (20), will influence the inherent force balance, resulting in the change of the morphologies. In the present study, we mainly discussed the effect of water content and nature of the common solvent on the self-assembly behaviors of PAzoM-b-PAA in THF/H_2O and DMSO/H_2O, respectively.

Figure 3(a) shows the TEM image of the PAzoM-b-PAA colloidal spheres obtained in THF/H_2O solution. As more and more water is added, the spheres transformed into vesicles with smaller and smaller diameters, which is shown in Figure 3(b, c and d). The interesting phenomenon is ascribed to the influence of water content. Water content affects both the shape and size of the copolymer aggregates. By increasing the water content, we can reduce the solvent quality for the PAzoM core. As more water is added, the solvent becomes poorer for the hydrophobic block and this results in an increase in the interfacial tension (described in the three factors earlier) between the core and the solvent outside the core. In response to the increased interfacial energy, there is an change in the morphologies (from spheres to vesicles) and vesicle sizes to minimize the total interfacial area, thus reducing the core-chain stretching and corona-chain repulsion.

Nevertheless, the self-assembly behaviors of PAzoM-b-PAA in DMSO/H_2O solution are different from those in THF/H_2O solution. Compared to THF/H_2O solution, PAzoM-b-PAA colloidal spheres with much smaller sizes

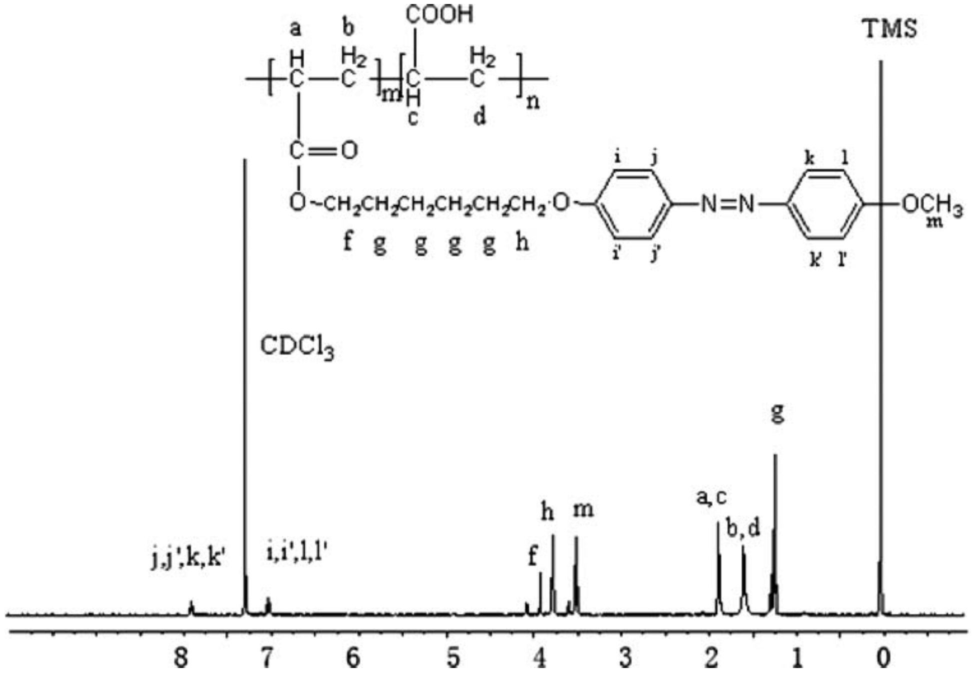


Fig. 2. ^{1}H-NMR spectrum of PAzoM-*b*-PAA in $CDCl_3$.

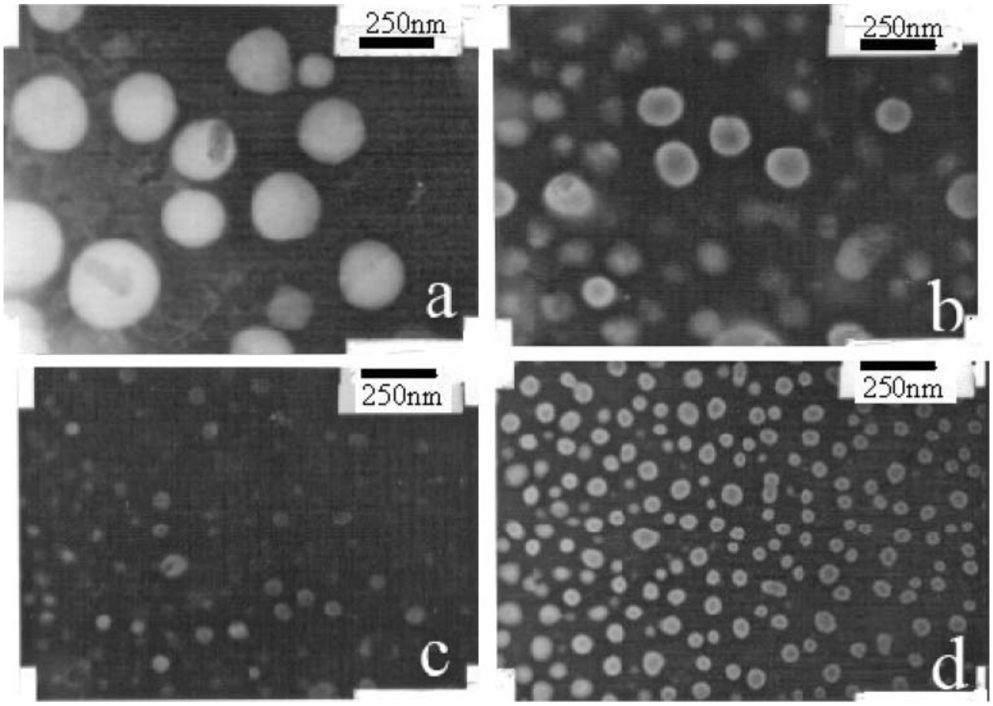


Fig. 3. TEM images of the colloidal spheres and vesicles composed of PAzoM-b-PAA in THF/H_2O solution with different water content (a) 60 vol%, (b) 70 vol%, (c) 80 vol%, (d) 90 vol%. The scale-bars in panels a–d are 250 nm.

(40–50 nm) are obtained when the initial solvent is DMSO at the same water content (60 vol%). In addition, the diameter of PAzoM-b-PAA spheres does not decrease obviously by continuous increase of the water content in DMSO. Besides, no aggregates of PAzoM-b-PAA vesicles are observed even if the water concentration is increased to 90 vol%, as it is shown in Figure 4. The above results are because of the effect of solvent.

The nature of the common solvent also has a major effect on the morphology of the aggregates. It is obvious that for an amphiphilic PAzoM-b-PAA copolymer, the interaction between the polymer chains and the solvent will influence the dimensions of both the aggregate core and the corona. On the one hand, the strength of the polymer- solvent interaction is related to the dielectric constant (ε). PAA and PAzoM are polar and the polarity of DMSO is higher than THF because of the higher dielectric constant of DMSO ($\varepsilon = 48.9$) than that of THF ($\varepsilon = 2.95$ (21). Therefore, the strength interaction between PAzoM-b-PAA and DMSO should be the stronger than that between PAzoM-b-PAA and THF. On the other hand, the repulsive interactions among the PAA corona chains

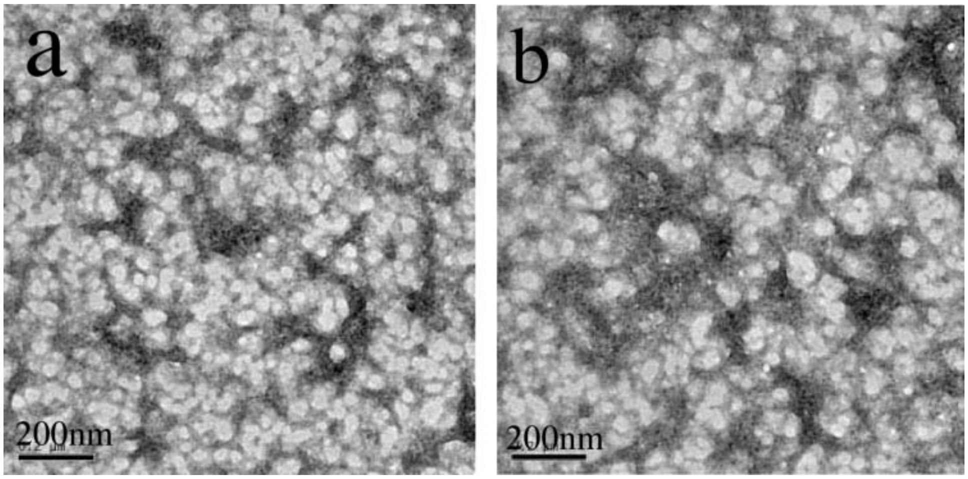


Fig. 4. TEM images of the colloidal spheres composed of PAzoM-b-PAA in DMSO/H_2O solution with different water content (a) 60 vol%, (b) 90 vol.%.

are related to the PAA-solvent interaction: the higher the strength of the PAA-solvent interaction, the higher the repulsion among the corona chains. From the polarity of DMSO and THF and the above analysis, it is apparent that the repulsive interaction among the PAA corona chains in DMSO is higher than that in THF. This results in a decrease of the aggregation number which, in turn, leads to a decrease of the dimension of the core and the degree of the stretching of PAzoM chains. In conclusion, because the strength of the PAA-DMSO interaction is stronger than that of PAA-THF, and the strength of the PAzoM-DMSO interaction is also stronger than that of PAzoM-THF, the spheres formed in DMSO had much smaller sizes (40–50 nm) than the spheres formed in THF.

The diameter of PAzoM-b-PAA spheres does not decrease obviously by continuous increase of the water content in DMSO. This result suggests that the effect of water content in the solution on the solvent content in the PAzom-rich phase is weaker in DMSO than in THF. The underlying reason for this behavior is the stronger interaction between the PAzom block and the DMSO vs. that in THF, so that more water is needed to remove the solvent from the PAzom-rich phase in THF than that in DMSO.

3.3 Photoisomerization of the PAzoM-b-PAA Diblock Copolymer

The trans-to-cis photoisomerization of the PAzoM-b-PAA diblock copolymer in the film and in the THF/H_2O suspension are studied, respectively. The film and the stable suspension of the PAzoM-b-PAA diblock copolymer are irradiated with 366 nm UV light until they reach the photostationary state. The spectra of both the film and the suspension change with different irradiation time (Figs. 5 and 6). The bands at 344 nm in the film and 355 nm in the suspension correspond to the $\pi - \pi^*$ transition of the PAzoM-b-PAA copolymer. The rate constants of isomerization are analyzed from the absorbance at 344 nm for the film and at 355 nm for the suspension, respectively. From the equation ln $(A_\infty - A_t)/(A_\infty - A_0) = -kt$ (22), the first-order rate constant of isomerization is determined, where A_t, A_0, and A_∞ are the absorbance at 344 nm or 355 nm at time t, time zero, and infinite time, respectively. In aqueous solution, the diblock copolymer self-assemble into core-shell micelles with the hydrophobic core formed by azo block. The formation of micelles shield the core azobenzene from the solvent water, and the core azobenzene is in a more hydrophobic environment than in the film. That is to say, the core azobenzene is in a less hydrophobic environment in film than in solvent.

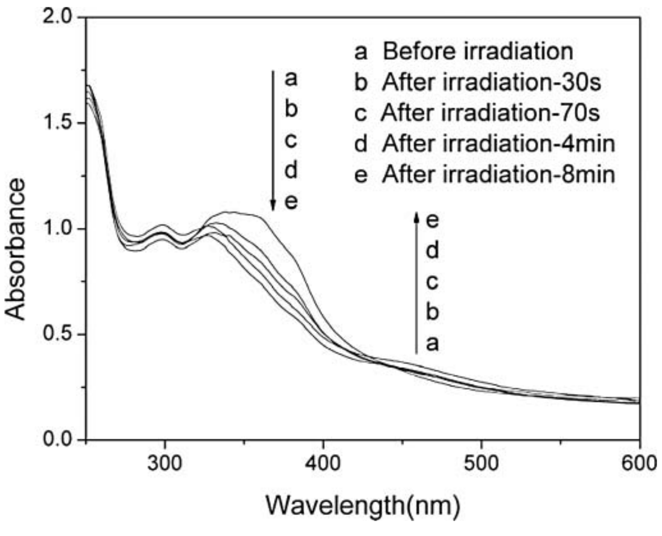


Fig. 5. UV-Vis spectra of the PAzoM-b-PAA film.

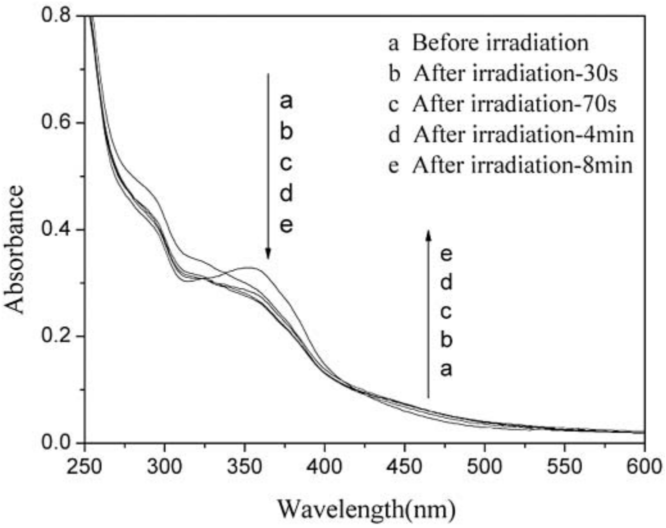


Fig. 6. UV-Vis spectra of PAzoM-b-PAA vesicles in THF/H_2O solution (90 vol.%).

According to previous study by Sin et al. (23), the thermal cis-transisomerization of azobenzene can proceed via two different mechanisms:(1) rotational mechanism involving rotation about the N—N bond and (2) inversion mechanism involving flip-flop inversion of one of the nitrogen atoms. The thermal cis-trans isomerization of azobenzene is slower in less hydrophobic environment if it proceed via the rotational mechanism (24, 25). As observed in the present study, the photoisomerization rate constant of PAzoM-b-PAA in the film (less hydrophobic environment) is found to be much lower ($k = 6.058 \times 10^{-3} s^{-1}$) than that in the THF/$H_2O$ suspension ($k = 1.107 \times 10^{-2} s^{-1}$), suggesting that a rotational mechanism might be operative for this water-soluble amphiphilic diblock copolymer (PAzoM-b-PAA). However, further studies are required for the confirmation of actual mechanism in future investigations.

4 Conclusions

A new amphiphilic azobenzene diblock copolymer is synthesized via reversible addition-fragmentation chain transfer polymerization in the hydrothermal reactor by inorganic hydrothermal synthesis method. Colloidal spheres are obtained through gradual hydrophobic aggregation of azobenzene diblock in THF/H_2O and DMSO/H_2O dispersion media, which is induced by continuous increase of water. The dielectric constant of the initial solvent plays an important role in the mophologies of PAzoM-b-PAA aggregates. PAzoM-b-PAA spheres transform into vesicles with decreased average diameter in THF/H_2O solution if more and more water is added. However, the water content is not the main factor to affect the morphology of the PAzoM-b-PAA aggregates in DMSO/H_2O solution. The lower photoisomerization rate constant of PAzoM-b-PAA in the film than in the THF/H_2O suspension indicates the rotational mechanism of the isomerization of PAzoM-b-PAA.

Acknowledgments

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