# Hybrid Colloids Composed of Two Amphiphilic Azo Polymers: Fabrication, Characterization, and Photoresponsive Properties

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ABSTRACT: This article reports the fabrication and characterization of a novel type photoresponsive colloids composed of two amphiphilic azo polymers. The colloids were built up by using an amphiphilic random azo copolymer (PEAPE) and a polydispersed azo homopolymer (BP-AZ-CA), which were functionalized with azobenzene type and pseudo-stilbene type chromophores, respectively. The colloids were prepared by gradually adding deionized water into a THF solution containing both PEAPE and BP-AZ-CA. In order to study the influence of the preparation conditions on the colloid composition and structure, the colloids were also prepared by mixing two THF−$H_2O$ solutions or dispersions of the polymers with different initial water content ($C_{w0}$) and then adding water into the mixture. When mixing the solutions with $C_{w0}$ below the critical water content (CWC), uniform colloidal spheres composed of the two polymers could be obtained. Upon irradiation of a linearly polarized $Ar^+$ laser beam, the hybrid colloidal spheres were deformed to "tadpole-like", "spindle-like", and other nonspherical structures depending on the composition of the colloids. As only the BP-AZ-CA component could be driven by the light irradiation, the photoinduced deformation degree increased with the increase of the active component in the hybrid colloids. When mixing the dispersions with $C_{w0}$ above CWC, the colloids obtained were observed to be a mixture of the hybrid colloids and monocomponent colloids. The photoisomerization study confirmed that the cores of the hybrid colloids were formed from the more hydrophobic PEAPE component, and the coronas were rich in the BP-AZ-CA component. The colloidal structures were formed due to the gradual hydrophobic aggregation of the polymeric chains in the THF-$H_2O$ media. In the forming process, the more hydrophobic PEAPE chains started to aggregate first and then BP-AZ-CA chains gradually assembled on the cores while the water content gradually increased. The understanding and methodology can be applied to construct colloids composed of two or more photoresponsive polymers or even other functional polymers.

## Introduction

Azobenzene and its derivatives have been widely used as dyestuffs, pigments, and pH indicators for a long time.[1] Recent studies show that polymers containing azobenzenes (azo polymers for short) can exhibit some fascinating photoresponsive variations such as phase transition,[2] chromophore orientation,[3] surface-relief-grating (SRG) formation,[4] photomechanical bending,[5] and many others.[6−9] The variations are triggered by the trans−cis photoisomerization of the azobenzenes.[10] The isomerization behavior of the azo chromophores plays a critical role in affecting the properties of azo polymers.[6,11] According to the differentiation at the isomerization behavior, the azo chromophores have been classified as azobenzene, amino-azobenzene, and pseudo-stilbene types.[12] For the azobenzene type chromophores, the cis-to-trans isomerization is relatively slow at room temperature, and the existence of the cis isomers can be easily detected by the spectroscopic method. This type of azo chromophore can be used as a molecular probe to detect the local environment surrounding it.[10] For amino-azobenzene type and pseudo-stilbene type molecules, the cis state of the molecules is relatively unstable, which relaxes back to the trans state at an extremely short time period. Upon light irradiation, the azo chromophore can rapidly undergo trans−cis−trans isomerization cycles, which can result in some accumulated and enlarged effects such as chromophore orientation.[3,6] The repeated trans−cis isomerization is also considered to be one of the key factors causing the SRG formation.[4] Various theoretical and spectroscopic methods have been used to study the potential energy surface and isomerization pathway of the azobenzenes at ground and excited states.[13] On the basis of the understanding, azo polymers with different photoresponsive properties can be designed and fabricated.

Colloidal particles, which have at least one dimension within the nanometer to micrometer range, are well-known as one of most important components used in many industrial products such as inks, paints, coatings, cosmetics, and photographic films, among others.[14] Recent studies have expanded the applications of the polymer-based colloids to new areas such as drug delivery, biodiagnostics, and combinatorial synthesis.[15−19] Monodispersed colloidal spheres can be used as building blocks to construct two-dimensional (2D) and three-dimensional (3D) ordered colloidal arrays.[20] The colloidal crystals can potentially be used in sensors, filters, optical switches, photovoltaic devices, soft lithographic processes, and photonic band gap (PBG) materials, among others.[21] Typically, colloids with narrow size distribution can be prepared by emulsion polymerization and self-assembly of block copolymers in a selective solvent. Emulsion polymerization can produce monodispersed latex particles of various polymers.[22] However, latex particles containing a large amount of azo chromophores can hardly be prepared by this method because of the inhibition of azo groups to the free-radical chain growth. To prepare uniform micellar spheres from block copolymers usually requires monodispersity of copolymers in both the molecular weight and block length.[23] Those well-defined copolymers can be prepared by the anionic living polymerization and controlled radical polymerizations such as atom transfer radical polymerization (ATRP).[8] Micellar aggregates have been prepared from amphiphilic diblock azo

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copolymers synthesized by ATRP.[24] The aggregates show interesting photoinduced deaggregation behavior caused by the photoisomerization of the azo chromophores. Recently, it has been reported by us that uniform colloidal spheres can be obtained from amphiphilic random azo copolymers or polydispersed homopolymers.[25,26] The colloidal spheres were formed through gradual hydrophobic association of the polydisperse polymer chains in aqueous−organic media induced by a continuous increase in the water content.[25] Depending on the chromophores tethered on the polymers, the colloidal spheres showed different photoresponsive properties. Upon exposure to linearly polarized $Ar^+$ laser single-beam or interfering beams, the colloidal spheres containing pseudo-stilbene type azo chromophores could be significantly stretched along the polarization direction.[26] The isomerization behavior of the colloidal spheres containing azobenzene type chromophores was studied by UV−vis spectroscopy, which supplied information about the local structure variation during the colloid formation.[25]

Colloids composed of more than one component can possess more complicated inner structure and combine interesting properties of those components. For low molecular weight surfactants, comicellization of multicomponents in aqueous solutions has been extensively studied.[27−35] Aggregation of diblock copolymers with different chain lengths and block compositions has also been reported.[36−40] As the aggregates have a compact core of the insoluble blocks surrounded by a loose shell of soluble blocks, the aggregates are usually named as micelles because of the structural similarities to the surfactant micelles. However, the block copolymer aggregates and low-molecular-weight surfactant micelles have significant differences in the formation mechanism. In comparison with micelles of low-molecular-weight surfactants, the kinetics of exchange between block copolymer in micelles and single chains in solution are far slower owing to the high viscosity of the insoluble blocks within the micelle cores.[23] In most cases, the cores of polymer micelles are regarded as "frozen" structures, lacking dynamic equilibrium between polymers in micelles and in the suspensions.[23e] Because even the block copolymers obtained by anionic polymerization may not be a true monodispersed system, the block copolymer micelles can be considered to consist of polymers with different chain lengths.[38] However, mixing two or more block copolymers with obviously different structure and molecular weight can hardly produce uniform micellar aggregates.[36−40] For amphiphilic random azo copolymers or polydispersed homopolymers mentioned above, the colloidal spheres are formed through a gradual hydrophobic association of the polymer chains in mixed aqueous−organic dispersion media.[25,26] In this self-assembling process, the most hydrophobic chains or segments start to aggregate at the critical water content (CWC). After that, other polymeric chains or segments gradually assembled on the cores according to their hydrophobicity as the water content gradually increases. This mechanism implies that colloids composed of different polydispersed polymers can be prepared through this self-assembly process. However, a report concerning the formation, structure, and properties of such hybrid colloids is still lacking in the literature.

In this work, the fabrication of the hybrid colloids composed of two amphiphlic azo copolymers (PEAPE and BP-AZ-CA) was investigated. PEAPE is a random copolymer containing azobenzene type chromophores, and BP-AZ-CA is an epoxy-based homopolymer bearing pseudo-stilbene type azo chromophores. The polymers were selected as the polymeric components because of their significantly different structures

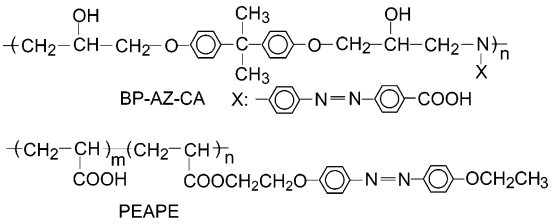


**Figure 1.** Chemical structure of PEAPE and BP-AZ-CA.

and photoresponsive properties. Constructing hybrid colloids composed of the two components were demonstrated on the basis of the gradual hydrophobic association scheme. Results indicated that the photoresponsive properties of the hybrid colloids were determined by the composition and preparation conditions. The hybrid colloid formation, structure, and properties are reported in this article in detail.

## Experimental Section

**Materials.** Analytical pure tetrahydrofuran (THF) from commercial source was refluxed with cuprous chloride and distilled for dehydration before use. Deionized water (resistivity >18 MΩ·cm) was obtained from a Millipore water purification system and used for the following experiments. Other reagents and solvents were used as received without further purification. PEAPE (its chemical structure is given in Figure 1) was prepared by the Schotten−Baumann reaction between poly(acryloyl chloride) (PAC) and 2-[4-(4-ethoxyphenylazo)phenoxy]ethanol (EAPE), and then the unreacted acyl chloride groups were hydrolyzed to obtain the carboxyl groups. As it was difficult to directly measure the molecular weight and its distribution of PAC due to the high reactivity of acyl chloride groups, the gel permeation chromatography (GPC) measurement was performed on a poly(methyl acrylate) sample that was prepared by the reaction between the same-batch synthesized PAC and excess methanol. The number-average degree of polymerization ($\overline{DP}$) of PAC estimated by the result of the poly(methyl acrylate) sample was 325 with a polydispersity index of 1.9. The PEAPE sample used in this study had the average degree of functionalization ($\overline{DF}$) of 47.8%, defined as the average percentage of the structure units bearing azo chromophores among the total units. The preparation and characterization details can be seen in our previous paper.[41] BP-AZ-CA (its chemical structure is given in Figure 1) was synthesized by the reaction between an epoxy-based precursor BP-AN and the diazonium salt of 4-aminobenzoic acid. The average degree of functionalization ($\overline{DF}$) was about 100%. The number-average molecular weight of the polymer was estimated to be 41 000 with the polydispersity index of 2.2. The preparation and characterization details of BP-AZ-CA can be seen in our previous paper.[42]

**Sample Preparation.** The hybrid colloids composed of PEAPE and BP-AZ-CA were prepared by a method similar to that used to obtain colloids containing a single polymeric component.[25,26] In a basic process, suitable amounts of PEAPE and BP-AZ-CA were premixed and dissolved in THF to obtain a solution with a total concentration of 0.4 mg/mL. Milli-Q water was added into the stirred THF solution at a rate of 5 $\mu$L/s. After the water content reached 80 vol %, the formed colloids were "quenched" by adding excess amount of water, and the suspension was dialyzed against water for 72 h to remove THF. To study the effect of the polymer concentration, a series of THF solutions containing both polymers were prepared, which had the concentrations in range from 0.05 to 0.5 mg/mL. For solutions containing two polymers, the initial polymer concentration ($C_{p0}$) mentioned in the following text refers to the total initial concentration of polymers in THF. The solutions were kept stirring for 20 min and then put aside for 72 h, and then the required amounts of water were added into the stirred THF solutions at a rate of 5 $\mu$L/s. For light scattering study, a series of solutions or dispersions of the polymers in the THF−$H_2O$ media with different water contents were prepared. After the water addition

was completed, the solutions or dispersions were left to equilibrate for at least 24 h. The light scattering measurement was performed on the solutions or dispersions to determine the parameters such as the critical water content (CWC) and the hydrodynamic radius ($R_h$). For preparation of the stable colloidal dispersions, water was further added into the polymer solutions or dispersions until the water content reached 80 vol %, and then the dispersions were "quenched" by adding excess water and dialyzed against water for 72 h to remove THF. To adjust the preparation conditions, PEAPE and BP-AZ-CA were separately dissolved in THF, and then Milli-Q water was added into the stirred THF solutions at a rate of 5 $\mu$L/s. When the water content of both solutions reached the required value, the solutions were mixed and Milli-Q water was added into the mixtures in the above-mentioned manner. After the total water content reached 80 vol %, the formed colloids were quenched by adding excess amount of water, and the suspensions were dialyzed against water for 72 h to remove THF.

**Characterization.** TEM images of the colloidal spheres were obtained by using a JEOL-JEM-1200EX electron microscope with an accelerating voltage of 120 kV. The TEM samples were prepared by dropping diluted sphere dispersions onto the copper grids coated with a thin polymer film and then dried in a 30 °C vacuum oven for 24 h. No staining treatment was performed for the measurements. Laser light scattering experiments were performed on a commercial LS instrument (ALV/DLS/SLS-5022F) equipped with a multi-$\tau$ digital time correlator (ALV/LSE-5003) and a solid-state laser (Uniphase, output power = 22 mW, at $\lambda$ = 632.8 nm). For estimating the average hydrodynamic radius ($R_h$) and polydispersity by dynamic light scattering (DLS), the cumulant method was used to describe logarithm of the total autocorrelation function as a series expansion, where the first cumulant ($\Gamma$) yields the *z*-averaged diffusion coefficient and the second cumulant ($\mu_2$) is a measure of polydispersity.[43] $R_h$ was obtained from the particle diffusion coefficient based on the Stokes−Einstein relation.[44] The static light scattering (SLS) was used to determine the critical water content (CWC) and the radius of gyration ($R_g$). The light scattering intensity used in the CWC measurements was a ratio of scattered light intensity to incident light intensity. The solutions used in LLS were clarified by a 0.45 $\mu$m Millipore filter. All the measurements were done at 20 ± 0.05 °C. The UV−vis absorption measurements were performed on a Perkin-Elmer spectrophotometer (Lambda Bio-40).

**Photoisomerization Study.** The photoisomerization of the azo chromophores was induced by irradiation with UV light, which was from a high-intensity 365 nm UV lamp equipped with 12.7 cm diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, U-09819-23 filter). The light intensity of the lamp was 7000 mW/cm$^2$ at a distance of 38 cm and 21 000 mW/cm$^2$ at a distance of 5 cm. The samples were placed at ca. 15 cm away from the lamp. The UV−vis spectra of the samples were measured over different irradiation time intervals by using an Agilent 8453 UV−vis spectrophotometer. To study the effect of the water content on photoresponsive behavior, the solutions or dispersions with different water contents were irradiated with the 365 nm UV light, and the UV−vis spectra were recorded over different time intervals until the photostationary states were achieved. For measuring the thermal cis-to-trans isomerization, the samples were kept in a dark oven with constant temperature (30 ± 1 °C), and the UV−vis spectra were recorded over different time intervals.

**Photoinduced Shape Deformation Study.** The samples for photoinduced shape deformation study were prepared by dropping diluted sphere dispersions onto the copper grids coated with a thin polymer film and then dried in a 30 °C vacuum oven for 24 h. A linearly polarized beam from an $Ar^+$ laser at 488 nm was used as the light source. The spatially filtered laser beam was expanded and collimated. The intensity of the laser beam was about 150 mW/cm$^2$. The linearly polarized laser beam was incident perpendicularly to the grid surfaces containing the colloids. The laser irradiation experiments were carried out at room temperature under an ambient condition. After the samples were irradiated for different time periods, the TEM observations were performed to detect the shape deformation.

## Results and Discussion

The chemical structure of PEAPE and BP-AZ-CA is given in Figure 1. PEAPE is an amphiphilic random copolymer functionalized with azobenzene type chromophores (4-hydroxyl-4′-ethoxyazobenzene (HEAZ) moieties). BP-AZ-CA is a homopolymer covalently bonded with pseudo-stilbene type azo chromophores (4-amino-4′-carboxylazobenzene (ACAZ) moieties). Both PEAPE and BP-AZ-CA could be completely dissolved in anhydrous THF to form homogeneous solutions with different concentrations. The hybrid colloids could be obtained by gradually adding water into a THF solution containing both polymers. To study the possible structure variation of the colloids, the polymers were also separately dissolved in THF, and a predetermined amount of water was added into each solution. After that, the solutions were mixed and colloids were obtained by adding more water into the mixture. The colloid formation, composition, and properties are related to the structural characteristics of the polymers and the preparation conditions. The results obtained from the preparation and characterization study will be presented in the following parts.

**Hybrid Colloid Preparation.** The most straightforward way to prepare the hybrid colloids was dissolving both polymers in THF and then gradually adding water into the solution. In a typical process, PEAPE and BP-AZ-CA (1:1, w:w) were dissolved in THF to obtain a homogeneous solution with a total initial concentration ($C_{p0}$) of 0.4 mg/mL, and then Milli-Q water was gradually added into the stirred THF solution. After the water content reached 80 vol %, the formed colloids were "quenched" by adding excess amount of water, and the suspension was dialyzed against water to remove THF. For comparison, the colloids containing single type polymers were prepared by the same method. Figure 2 shows some typical TEM images of the colloids, which were obtained from the stable dispersions of PEAPE (Figure 2a), BP-AZ-CA (Figure 2b), and PEAPE/BP-AZ-CA (1:1 w:w) colloids (Figure 2c). The colloids all appear as uniform colloidal spheres. The hybrid colloidal spheres possess a more uniform shape compared with the monocomponent colloids.

The dynamic light scattering (DLS) was used to determine the average hydrodynamic radius ($R_h$) and polydispersity of colloidal spheres in the aqueous dispersions.[44] Figure 3 shows the size distribution curves of the PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA (1:1, w:w) colloids. The hybrid colloids have an obviously lower polydispersity (0.061) compared with both the PEAPE colloids (0.138) and the BP-AZ-CA colloids (0.156), which is consistent with the TEM observation. The static light scattering (SLS) was used to determine the radius of gyration ($R_g$).[45] Table 1 summarizes the $R_h$, $R_g$, and $R_g/R_h$ of the colloidal spheres of PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA. The $R_h$ of the PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA colloids is 154, 102, and 111 nm and the $R_g$ is 119, 79, and 86 nm, respectively. The $R_g/R_h$ value can be used to characterize the shape of the colloids.[46,47] $R_g/R_h$ estimated for the above samples is all around 0.775, which confirms that the colloids are spherical particles in the suspensions.

Both TEM observation and DLS study show that the hybrid colloids could be obtained from the solution containing different ratios of PEAPE and BP-AZ-CA. Generally, the hybrid colloids are more uniform and have narrower size distribution than the monocomponent colloids. When the ratio of PEAPE to BP-AZ-CA is in range from 50:50 to 70:30 (w:w), the hybrid colloids with smaller size and the narrowest size distribution

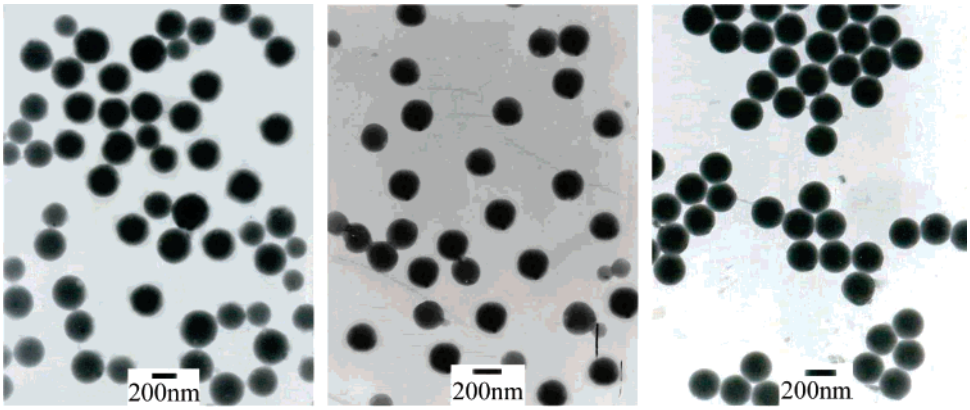


**Figure 2.** Typical TEM images of the colloidal spheres: (a) PEAPE, (b) BP-AZ-CA, and (c) PEAPE/BP-AZ-CA (1:1, w:w).

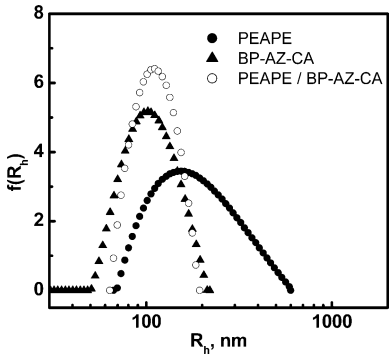


**Figure 3.** Distribution of the hydrodynamic radius ($R_h$) of the colloidal spheres of PEAPE, BP-AZ-CA and PEAPE/BP-AZ-CA (1:1, w:w) in the aqueous dispersions.

**Table 1. DLS and SLS Experimental Results for the Colloidal Spheres Dispersed in Water**[a]

| samples | $R_h$ (nm) | $\mu_2/\Gamma^2$ | $R_g$ (nm) | $R_g/R_h$ |
|---|---|---|---|---|
| PEAPE | 154 | 0.138 | 119 | 0.775 |
| BP-AZ-CA | 102 | 0.156 | 79 | 0.775 |
| PEAPE/BP-AZ-CA | 111 | 0.061 | 86 | 0.775 |

[a] Here $\mu_2/\Gamma^2$ is the polydispersity index of the colloids dispersed in the water, measured by DLS.

can be obtained (Figure S1, in the Supporting Information; also see TEM images given in Figure 9a−d).

**Effect of Water Content on Colloid Formation.** The formation process of the hybrid colloids can be understood by studying the relationship between the polymer chain association and the water content in the media. For the purpose, the critical water content (CWC) was used to characterize the water content at which polymer chains start to associate. CWC can be obtained from the turning-up point on the plot of the light-scattering intensity vs the water content in the medium.[48,49] CWC is related to the hydrophobicity of the polymers and the initial polymer concentration ($C_{p0}$) in the organic solvent. CWCs were measured by the light scattering performing on the solutions containing two components (PEAPE/BP-AZ-CA) and a single component (PEAPE or BP-AZ-CA) with different $C_{p0}$. When water was gradually added into the solutions, an abrupt increase in the scattered light intensity was observed, which indicated that polymer chains started to associate in the solutions caused by the hydrophobic interaction. Figure 4 gives the plots of the light scattering intensity of the PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA (1:1, w:w) solutions vs the water content, where $C_{p0}$ is 0.4 mg/mL. The PEAPE solution shows a far lower CWC

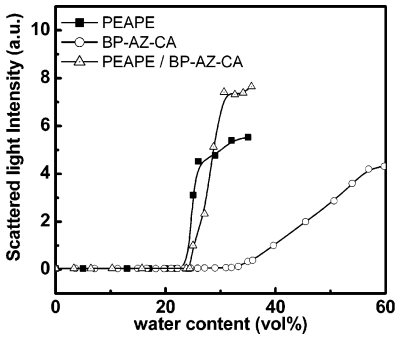


**Figure 4.** Scattering light intensity as a function of the water content (vol %) for PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA (1:1, w:w) dissolved in THF-$H_2O$ media. The scattered light intensity shown here is a ratio of scattered light intensity to incident light intensity.

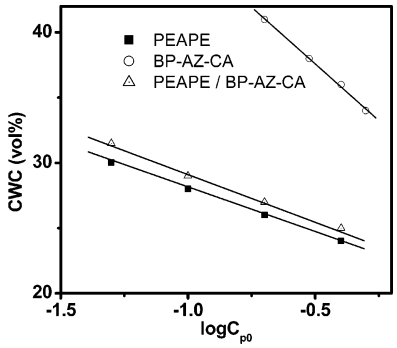


**Figure 5.** Plots of the critical water content (CWC) vs logarithm of the initial polymer concentration ($C_{p0}$) for PEAPE, BP-AZ-CA, and PEAPE/BP-AZ-CA (1:1, w:w) in THF.

(24 vol %) compared with that of the BP-AZ-CA solution (36 vol %). For the PEAPE/BP-AZ-CA solution, the sudden increase in scattered light intensity occurs at the water content of 25 vol %. The CWC of the PEAPE/BP-AZ-CA solution is close to that of PEAPE.

As the $C_{p0}$ increased, a decrease of the CWC was observed for the solutions containing PEAPE/BP-AZ-CA (1:1, w:w) and its corresponding monocomponent counterparts. Similar to block copolymer system,[48] CWC was observed to decrease linearly as $C_{p0}$ logarithmically increases (Figure 5). The relationship can be fitted by the following equation:

$$\mathrm{CWC} = -A \log C_{p0} + B \qquad (1)$$

where $A$ and $B$ are two constants and need to be determined for a specific polymer system. The result also shows that the

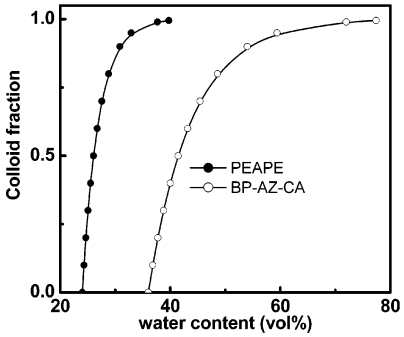


**Figure 6.** Fraction of the associated chains of PEAPE and BP-AZ-CA as a function of the water content.

solutions containing PEAPE/BP-AZ-CA and containing PEAPE have a similar relationship between CWC and the logarithm of $C_{p0}$. The results given in Figure 4 and 5 imply that in the PEAPE/BP-AZ-CA solutions more hydrophobic PEAPE chains start to aggregate first, and the CWC of the solutions is determined by the more hydrophobic PEAPE component.

For PEAPE and BP-AZ-CA, the influence of the water content on chain association fraction can be estimated by using a method proposed by Eisenberg et al. to calculate the micelle fraction of amphiphilic block copolymers.[48] The fraction of the associated chains as a function of the water content can be estimated by

$$(C_{p0} - C_{unass})/C_{p0} = 1 - \exp(-2.303\Delta H_2O/A) \quad (2)$$

where $C_{unass}$ represents the concentration of the unassociated polymer chains in the solution and $\Delta H_2O$ represents the increment of added water above CWC.[49] The constant $A$, whose value depends on specific polymer and organic solvent, can be obtained from the slope of the plot of CWC vs log $C_{p0}$ (Figure 5).[48,49] By using eq 2, the change of $(C_{p0} - C_{unass})/C_{p0}$ as a function of the $H_2O$ increment was calculated. The plots of $(C_{p0} - C_{unass})/C_{p0}$ against $\Delta H_2O$ are shown in Figure 6, where the initial polymer concentration is 0.4 mg/mL. For PEAPE, the percentage of the associated chains is estimated to be 99.5% when the water content reaches 40 vol % (i.e., $\Delta H_2O = 16$ vol %). As mentioned above, BP-AZ-CA polymer chains start to associate at 36 vol % (CWC). Only when the water content reaches 77 vol % (i.e., $\Delta H_2O = 41$ vol %) can the percentage of the associated chains reach 99.5%.

For the dispersions containing both polymers, the variation of aggregation fraction vs the $H_2O$ increment cannot be directly calculated by using eq 2. Although the interaction between the PEAPE and BP-AZ-CA molecules could cause some deviation, the tendency given in Figure 6 should be correct at least semiquantitatively. It means that a significant amount of PEAPE chains in the dispersion have associated when BP-AZ-CA chains start to associate. If the less hydrophobic BP-AZ-CA chains assemble on the PEAPE-dominated cores as the water content further increases, hybrid colloids containing both polymers can be obtained. This nucleation and growth scheme is supported by the photoresponsive behavior study that will be presented in the following parts.

**Possible Structure Variation.** To further explore the colloid formation mechanism and possible structure variation, the colloids were also prepared by mixing the polymer solutions or dispersions containing a predetermined amount of water. In the process, PEAPE and BP-AZ-CA were separately dissolved in THF, and a suitable amount of water was added into the solutions to form PEAPE/THF-$H_2O$ and BP-AZ-CA/THF-$H_2O$ solutions or dispersions. A series of solutions or dispersions

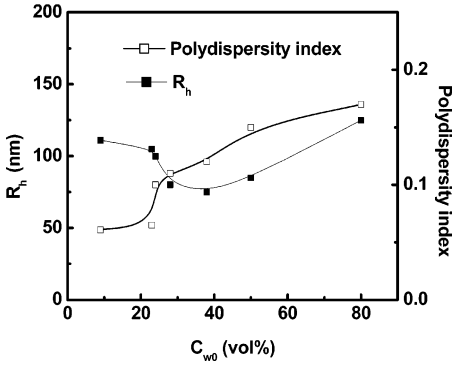


**Figure 7.** Hydrodynamic radius ($R_h$) and polydispersity index of the colloidal spheres, which were obtained by adding water into PEAPE/BP-AZ-CA solutions or dispersions with different $C_{w0}$.

with different water contents were prepared in this way. Each of the solutions or dispersions represented a special growing stage of the colloid formation. By mixing PEAPE/THF-$H_2O$ and BP-AZ-CA/THF-$H_2O$ solutions or dispersions with the same water content, a solution or dispersion having this initial water content was obtained. In the following parts, the initial water content ($C_{w0}$) refers to the water content at which the PEAPE/THF-$H_2O$ and BP-AZ-CA/THF-$H_2O$ solutions or dispersions were mixed. The colloids of the polymers were then obtained by gradually increasing the water content in the media. After the water content in the media reached 80 vol %, the structures formed in the suspensions were "quenched" by adding excess water, and the suspensions were dialyzed against water to remove THF.

According to the results given in above section, the mixed solutions or dispersions can be divided into several different initial states depending on the $C_{w0}$. For the THF solution with the $C_{p0}$ of 0.4 mg/mL, PEAPE and BP-AZ-CA start to associate at the water contents of 24 and 36 vol % (CWC), and almost all polymer chains are involved in the aggregates when the water contents reach 40 and 77 vol %, respectively. If not considering the mutual interaction between the two components, the mixed solutions or dispersions can have the following states. When $C_{w0}$ is lower than 24 vol %, chains of both polymers exist in the "isolated" state in the solutions. When $C_{w0}$ is between 24 and 36 vol %, more or less PEAPE chains are associated and BP-AZ-CA still exist as the "isolated" chains. When $C_{w0}$ is between 36 and 40 vol %, almost all PEAPE chains and only a small fraction of BP-AZ-CA chains are involved in the aggregates. When $C_{w0}$ is higher than 40%, all of the PEAPE chains are aggregated, and the amount of the associated BP-AZ-CA chains depends on the water content. When $C_{w0}$ is higher than 77%, both PEAPE and BP-AZ-CA are involved in their own aggregates. Therefore, it can be expected that by altering the $C_{w0}$ the colloid composition and structure can be adjusted.

TEM observation showed that colloids obtained with the different $C_{w0}$ values all appear as spherical particles. Figure 7 shows $R_h$ and polydispersity of the colloidal spheres varying with $C_{w0}$, which were obtained by DLS performed on the stable water dispersions containing the colloids. When $C_{w0}$ is below 24 vol %, the colloids have narrow size distribution. In this range, $R_h$ and polydispersity show a slight change with the $C_{w0}$ variation. $R_h$ significantly decreases when $C_{w0}$ increases in the range from 24 to 36 vol %. The polydispersity abruptly increases when $C_{w0}$ in the range from 24 to 28 vol %. When $C_{w0}$ is higher than 40 vol %, both $R_h$ and polydispersity increase as $C_{w0}$ increases. As will be clarified by the photoresponsive behavior study, the colloids obtained in the different $C_{w0}$ ranges can be

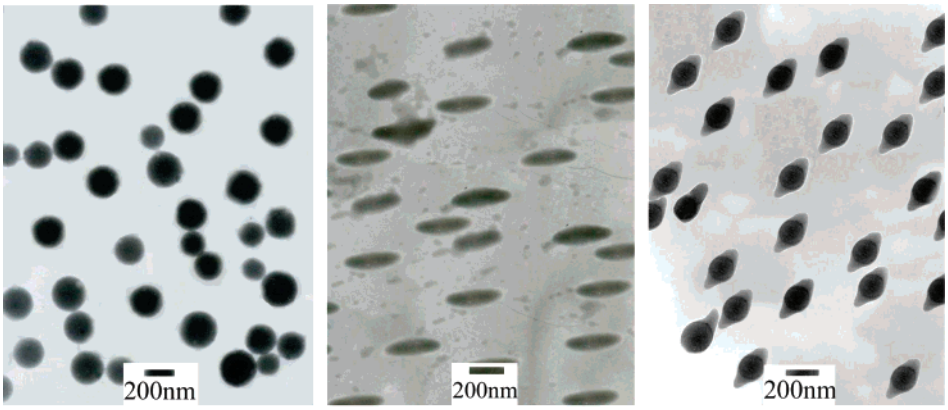


**Figure 8.** TEM images the colloids after exposed to a linearly polarized $Ar^+$ laser beam for different time periods: (a) PEAPE, 2 h; (b) BP-AZ-CA, 20 min; (c) PEAPE/BP-AZ-CA (1:1, w:w), 2 h.

aggregates with different compositions, which are caused by the different nucleation and growth processes.

**Photoinduced Deformation and Colloid Composition.** The hybrid colloids can show photoinduced deformation upon the relative amount of the BP-AZ-CA component. The colloid composition variation caused by the $C_{w0}$ change can be identified by the study on the photoinduced shape deformation. The samples for the study were prepared by dropping diluted colloidal dispersions onto the copper grids coated with a thin polymer film. A linearly polarized $Ar^+$ laser beam at 488 nm with intensity of 150 mW/cm$^2$ was used as the light source. The colloidal spheres were exposed to the spatially filtered and collimated laser beam incident perpendicularly on the substrate surfaces. The morphologies of colloidal spheres were observed by TEM before and after the laser irradiation. For comparison, the hybrid colloids prepared under different conditions and the monocomponent colloids were studied in the same way.

Figure 8 gives the TEM images of the colloidal spheres after the light irradiation. The TEM images of the colloidal spheres before light irradiation have been given in Figure 2. There is no observable shape deformation for PEAPE colloids after being irradiated for 2 h (Figure 8a). The BP-AZ-CA colloidal spheres can be significantly elongated along the light polarization direction (Figure 8b), after being irradiated for 20 min. The deformation behavior has been reported in our previous paper.[26] For the hybrid colloids, the spheres can be deformed to "spindle-like" or "tadpole-like" particles with dark spherical cores (Figure 8c). Obviously, after the light irradiation, the hybrid colloids show unique deformation morphology and a lower deformation degree compared with the BP-AZ-CA colloids.

Figure 9 shows the TEM images of the hybrid colloids containing different amount of BP-AZ-CA before the light irradiation and after exposure to the linearly polarized $Ar^+$ laser beam for 2 h. Before the light irradiation, the colloids all appear as uniform spheres (Figure 9a−d). The hybrid colloids containing 80 wt % of BP-AZ-CA show a similar shape deformation as BP-AZ-CA colloids (Figure 9e), although the degree of deformation is less for the same irradiation time period. For the hybrid colloids containing 20 wt % of BP-AZ-CA, the same light irradiation can only cause a much less degree of the deformation (Figure 9h). For the hybrid colloids containing 40 and 60 wt % of BP-AZ-CA (Figure 9f,g), a similar shape deformation like that given in Figure 8c can be observed.

The above results confirm that uniform colloidal spheres composed of the two polymers have been obtained. The colloidal spheres formed from BP-AZ-CA can exhibit significant deformation upon $Ar^+$ laser irradiation, while PEAPE colloids do not show such deformation under the same condition. When the colloids are obtained from a THF solution containing both polymers, all particles show very similar deformation upon the light irradiation and the deformation degree is lower than the BP-AZ-CA colloids. This result clearly indicates that both BP-AZ-CA and PEAPE components are involved in the colloids. The formation of the hybrid colloidal spheres can be explained by the gradual hydrophobic association scheme.[25] When the water content is lower than CWC, both polymers are homogeneously dissolved in the solvents. When the water content reaches CWC, only the most hydrophobic fraction of the PEAPE chains meets the phase separation condition and starts to aggregate. For the PEAPE/BP-AZ-CA solution with $C_{p0}$ equal to 0.4 mg/L, PEAPE starts to associate at the CWC of 25 vol %. Those most hydrophobic chains or segments form the cores of the hybrid colloidal spheres. When the water content further increases, more and more polymer chains meet the phase separation condition and transfer from the solution into the aggregates. Those polymer molecules gradually assemble on the cores, which is the colloidal sphere growth process. In this gradual growth process, the more hydrophobic PEAPE chains compose the inner parts and the BP-AZ-CA chains form the shells.

For the colloidal spheres prepared by mixing the PEAPE/THF-$H_2O$ and BP-AZ-CA/THF-$H_2O$ solutions or dispersions, the photoinduced deformation behavior depends on the $C_{w0}$. Figure 10a−d shows the TEM images of the colloidal spheres after exposed to a linearly polarized $Ar^+$ laser beam for 2 h, where the colloids were obtained from systems with some representative $C_{w0}$, and $C_{p0}$ is fixed to be 0.4 mg/mL. When $C_{w0}$ is below or even equal to 24 vol % (CWC of PEAPE), all colloidal spheres can be deformed by the light irradiation (Figure 10a,b). The deformed colloids show the "tadpole-like" or "spindle-like" shapes. When $C_{w0}$ is 28 vol %, the irradiated colloids show three very different morphologies, i.e., unaffected spheres, "tadpole-like", or "spindle-like" colloids, and the completely deformed colloids (Figure 10c). By comparing the images given in Figures 8 and 9, the colloids can be identified as the PEAPE-dominated colloids, PEAPE/BP-AZ-CA hybrid colloids, and BP-AZ-CA dominated colloids, respectively. When $C_{w0}$ is 80 vol %, only two type morphologies can be observed (Figure 10d), which correspond to the PEAPE colloids and BP-AZ-CA colloids.

These different situations are directly related to the $C_{w0}$, which can be understood by considering its influence on the composi-

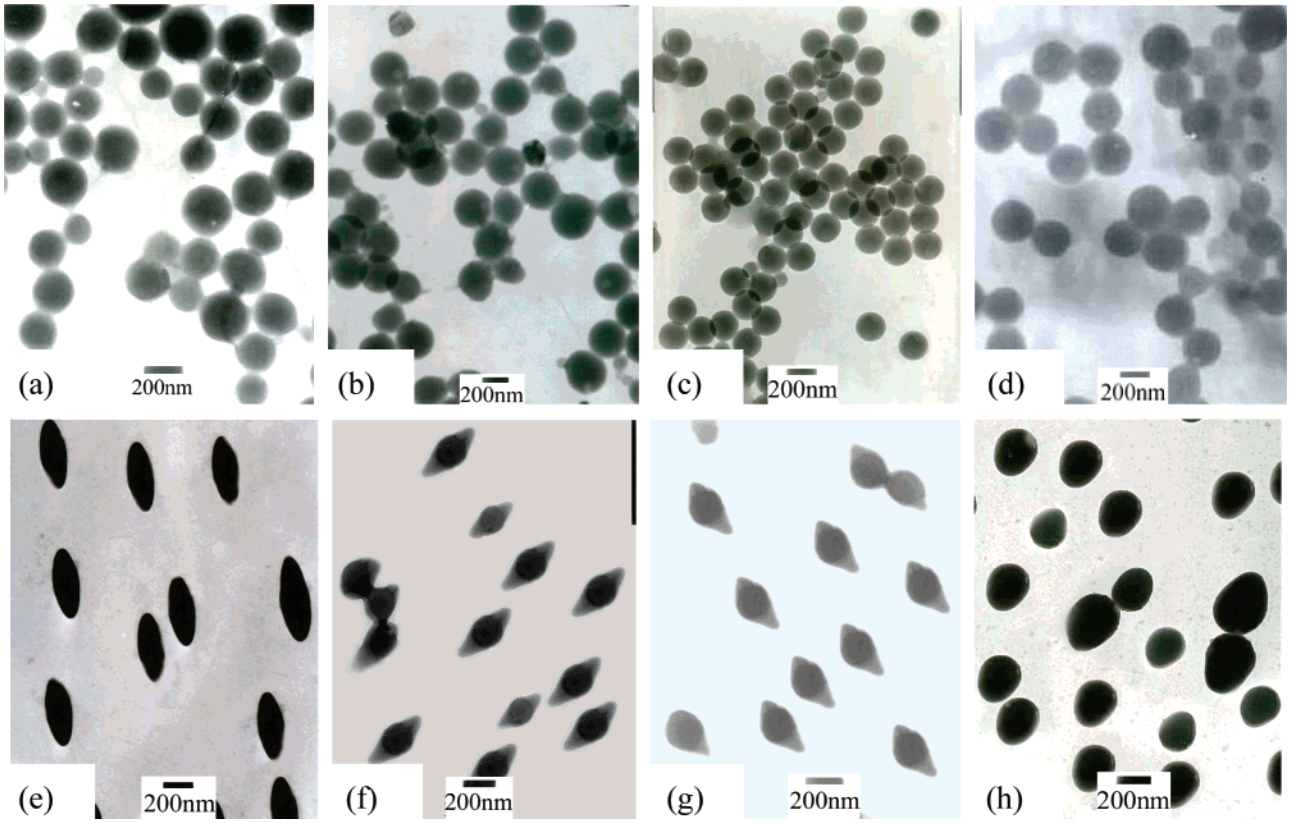


**Figure 9.** Typical TEM images of the PEAPE/BP-AZ-CA colloids containing a different percentage of PEAPE before and after the $Ar^+$ laser irradiation for 2 h: (a) 20 wt %, before irradiation; (b) 40 wt %, before irradiation; (c) 60 wt %, before irradiation; (d) 90 wt %, before irradiation; (e) 20 wt %, after irradiation; (f) 40 wt %, after irradiation; (g) 60 wt %, after irradiation; (h) 90 wt %, after irradiation.

tion of the colloids. When $C_{w0}$ is below 24 vol %, the colloids formed from the mixture show similar photoinduced shape deformation as those obtained from the THF solution. In this case, PEAPE and BP-AZ-CA are homogeneously dissolved in the mixed solutions, and the colloids form through the hydrophobic association process involving both polymers. When $C_{w0}$ is over 80 vol %, the colloids obtained are a mixture of two different type colloids: one is mainly composed of PEAPE, and the other is mainly composed of BP-AZ-CA. At the initial moment when the two dispersions are mixed, the two type polymers are already involved in their own aggregates, and the component exchange between the aggregates is too slow to cause a significant component variation. Adding water into the mixture only results in the "freezing" of the colloidal structure, which are composed of the PEAPE or BP-AZ-CA components separately. When an intermediate $C_{w0}$ is adopted, more complicated situations have been observed. When the solutions of PEAPE and BP-AZ-CA with $C_{w0}$ of 28 vol % are mixed, three different type colloids (the hybrid colloids and colloids mainly containing PEAPE or BP-AZ-CA) are observed. In this case, when two solutions are mixed, a part of PEAPE chains are involved in the aggregates, and BP-AZ-CA chains are still in the "isolated" state. While water is gradually added into the system, the colloid nucleation and growth can involve some diversified processes, such as growth on the PEAPE nuclei, formation of new nuclei of PEAPE or BP-AZ-CA, and growth on the newly formed nuclei. The processes depend on the factors such as the nucleation energy barrier, compatibility of the components, charge interaction, and surface tension as well as the composition. The involved influence of $C_{w0}$ on the $R_h$ and polydispersity of the colloids (given in Figure 7) can be partially understood by considering the complication. To clarify the full relationship between the factors will require more investigations both experimentally and theoretically.

**Photoisomerization of Azo Chromophores.** The top curves in Figure 11a,b show the UV−vis spectra of the stable suspensions of the PEAPE/BP-AZ-CA (1:1, w:w) hybrid colloids, obtained from a THF solution and a solution with $C_{w0}$ equal to 24 vol %. For single component colloids of PEAPE and BP-AZ-CA, the $\pi-\pi^*$ bands ($\lambda_{max}$) appear at 365 and 470 nm (Figure S2, in the Supporting Information). For the hybrid colloids, the absorption bands appearing at 365 and 455 nm belong to the HEAZ and ACAZ moieties of the polymers. The new band appearing at 387 nm could be assigned to the charge-transfer absorption from the HEAZ/ACAZ charge-transfer complex. As the photoisomerization of azobenzenes is sensitive to the local environment surrounding them, information about the inner structure can be obtained by measuring the isomerization rate.[10,25] As mentioned above, BP-AZ-CA and PEAPE are covalently bonded with the pseudo-stilbene type azo chromophores (ACAZ moieties) and azobenzene type chromophores (HEAZ moieties), respectively. As only the photoisomerization of azobenzene type chromophores can be monitored by ordinary UV−vis spectroscopy,[6b,12] it was investigated to probe the local environment surrounding the HEAZ moieties.

The colloid suspensions were irradiated with 365 nm UV light for different time periods, and the UV−vis spectra of the samples were recorded until the photostationary states were achieved. Figure 11 shows two typical series of the UV−vis spectra. Upon the light irradiation, the absorption at 365 and 387 nm decreases gradually as the result of the trans-to-cis isomerization of the HEAZ chromophores. As ACAZ is a pseudo-stilbene type chromophore, its trans−cis isomerization is too fast to be detected at the time scale given in this work.[12]

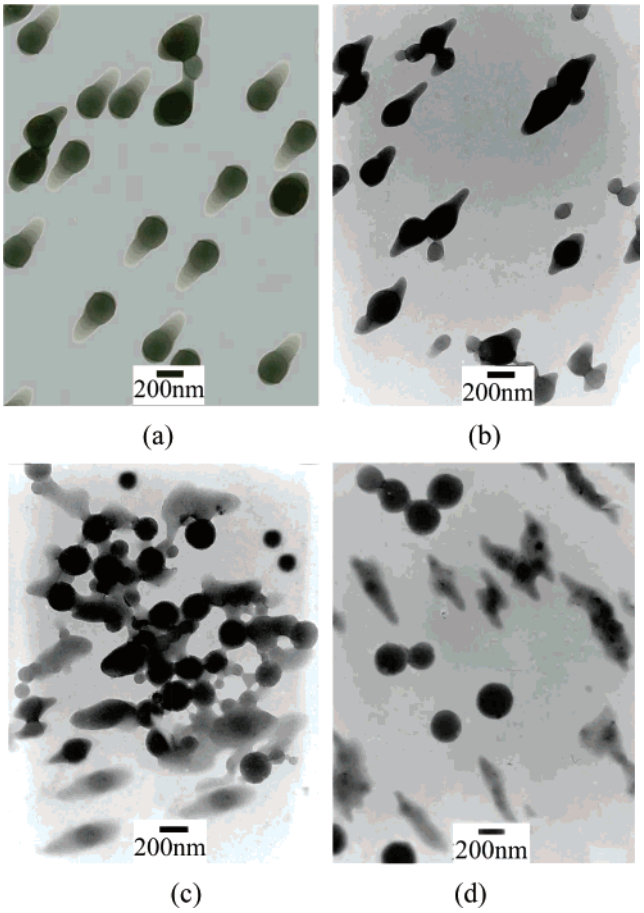


**Figure 10.** Typical TEM images of the colloids after exposed to a linearly polarized $Ar^+$ laser beam for 2 h. The colloids were obtained by adding water into the solutions or dispersions with the $C_{w0}$ equal to (a) 9, (b) 24, (c) 28, and (d) 80 vol %.

Therefore, no variation is observed for its absorption band at 455 nm. From the figures, the absorbance at 365 nm before the light irradiation ($A_{origin}$), and the absorbance at the same wavelength after the irradiation for different time periods ($A_t$) can be obtained. The relative absorbance ($A_t/A_{origin}$) of the samples can be used to indicate the relative amount of the trans isomers remaining at $t$ time. The variations of $A_t/A_{origin}$ with $t$ represent the kinetics of the photoisomerization. The variations can be best fitted by the first-order exponential decay function

$$A_t/A_{origin} = A_0 + A_1 \exp(-t/T_1) \quad (3)$$

where $T_1$ is the characteristic time of the decay process. For comparison, the photoisomerization behavior of a stable dispersion of the PEAPE colloids was studied in the same way (Figure S3, in the Supporting Information). Both experimental data and fitting curves are shown in Figure 12. $T_1$ obtained from the curve fitting are 43.4 and 50.7 s for the colloids obtained from a THF solution and a solution with $C_{w0}$ equal to 24 vol %. For the PEAPE colloid sample, $T_1$ was measured to be 37.3 s. Comparing with the monocomponent PEAPE colloids, the trans-to-cis isomerization rate is far slower for the hybrid colloids (Table 2). As mentioned above, for the systems prepared from the dispersions with a higher $C_{w0}$ (such as 28 vol %, for $C_{p0}$ equal to 0.4 mg/mL), the composition of the colloids can be diversified. As other effects such as "screen effect" could cause problem to clearly interpret the result, the photoisomerization behavior of the systems will not be presented here.

The result obtained from the photoisomerization study is consistent with the results discussed in the other parts of this paper. As mentioned in the last section, although the hybrid colloids can be deformed by the light irradiation, TEM observation shows that the deformed shape is different to the BP-AZ-CA colloids. A typical appearance shows a circle core with

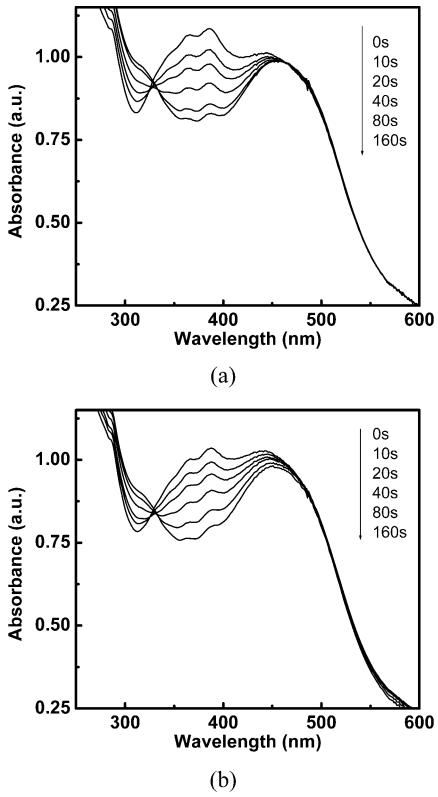


**Figure 11.** Variation of the UV−vis spectra of the colloidal dispersions induced by the UV light irradiation. The dispersions were obtained by adding water into (a) a THF solution of PEAPE/BP-AZ-CA (1:1, w:w) and (b) a THF-$H_2O$ solution of PEAPE/BP-AZ-CA (1:1, w:w) with $C_{w0}$ of 24 vol %.

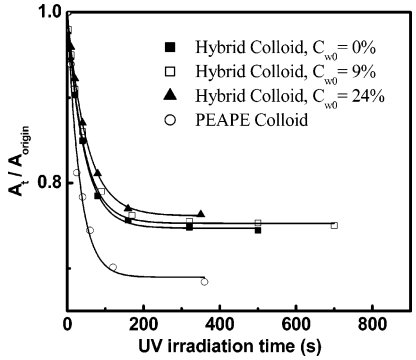


**Figure 12.** Plot of the relative absorbance ($A_t/A_{origin}$) varying with the irradiation time and the fitting curves for dispersions containing PEAPE/BP-AZ-CA (1:1, w:w) colloids, prepared by adding water into the THF-$H_2O$ solutions with different $C_{w0}$. The data and fitting curve for PEAPE colloidal dispersion are also given for comparison.

**Table 2. Parameters of the Photoisomerization Kinetics Obtained from the Curve Fitting for the PEAPE Colloids and Hybrid Colloids[a]**

| sample | $A_0$ | $A_1$ | $T_1$(s) | $\chi^{2\,b}$ |
|---|---|---|---|---|
| HC[c] ($C_{w0}$ = 0%) | 0.75 | 0.26 | 43.4 | $8.1 \times 10^{-6}$ |
| HC[c]($C_{w0}$ = 9%) | 0.75 | 0.25 | 45.2 | $8.0 \times 10^{-5}$ |
| HC[c] ($C_{w0}$ = 24%) | 0.76 | 0.24 | 50.7 | $1.2 \times 10^{-5}$ |
| PEAPE colloid | 0.69 | 0.31 | 31.8 | $2.3 \times 10^{-4}$ |

[a] The hybrid colloids were prepared by adding water into the PEAPE/BP-AZ-CA (1:1, w:w) solutions with different $C_{w0}$. [b] Here $\chi^2$ is the mean squared error of the fitting. [c] Hybrid colloids.

higher contrast and tails stretched from the core. By comparing the photoresponsive behavior of both polymers, it can be concluded that the cores and tails are composed of PEAPE and BP-AZ-CA, respectively. The result also implies that the PEAPE and BP-AZ-CA components in the colloids are not mixed with each other at the molecular level. Only in this case can light force drive the BP-AZ-CA component out of the colloids. The photoisomerization rate is obviously lower for the hybrid colloids than that of the PEAPE colloids, which also indicates that the PEAPE component consists of the cores of the hybrid colloids. Compared with the PEAPE colloids, where a fraction of HEAZ chromophores distributes in the shells, the free volume for the photoisomerization is reduced if PEAPE chains are mainly confined in the cores of the hybrid colloids. By comparing the three types of the hybrid colloids obtained for the solutions with $C_{w0}$ equal to 0, 9, and 24 vol %, the photoisomerization rate decreases as the $C_{w0}$ increases. This result can be explained by considering that a small amount of preassociated PEAPE chains can act as the "seeds" as the $C_{w0}$ increases, which causes more PEAPE chains to be involved in the cores.

## Summary

A novel type photoresponsive colloid has been created by using two amphiphilic azo polymers (PEAPE and BP-AZ-CA), which possess different hydrophobicity. Uniform colloidal spheres were fabricated by dissolving both polymers in THF or a THF-$H_2O$ medium with $C_{w0}$ below CWC and then gradually adding water into the solutions. By selecting a suitable PEAPE content in the mixture, more uniform colloids with a narrow size distribution could be obtained. The light scattering study indicated that when the water content increased, more hydrophobic PEAPE chains started to aggregate before BP-AZ-CA chains involved in the process. The hybrid colloids showed shape deformation upon the linearly polarized $Ar^+$ laser irradiation. The photoinduced deformation degree increased with the increase of the BP-AZ-CA component in the colloids. Upon UV light irradiation, the hybrid colloids showed a photochromic effect related to the photoisomerization of the PEAPE component in the colloids. The above results indicate that the colloidal spheres have a core formed from the more hydrophobic PEAPE chains and corona mainly composed of the more hydrophilic BP-AZ-CA chains. The structure is formed by the gradual hydrophobic aggregation of the polymeric chains in the THF-$H_2O$ dispersion media. On the basis of the understanding, colloidal spheres with a narrower size distribution can be prepared by using more than one carefully selected polymer component. Multifunctional colloids can be designed and prepared by combining polymers with different properties.

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**Supporting Information Available:** Plots of $R_h$ and polydispersity vs the hybrid colloid composition, the UV−vis spectra of the PEAPE and BP-AZ-CA colloids, and the UV−vis spectra of the PEAPE colloids before and after the UV light irradiation for different time periods. This material is available free of charge via the Internet at http://pubs.acs.org.

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