# Influence of chromophoric electron-withdrawing groups on photoinduced deformation of azo polymer colloids

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## ARTICLE INFO

## ABSTRACT

This study investigated the influence of chromophoric electron-withdrawing groups on photoinduced deformation behavior of colloidal spheres of three azo polymers. The colloidal spheres were prepared by using the epoxy-based azo polymers (BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT) through gradual hydrophobic aggregation of the polymers in THF–H$_2$O media. The colloidal spheres were controlled to have similar average sizes by adjusting both the polymer concentrations in the initial THF solutions and water-adding rates in the preparation processes. The colloids were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The colloid deformation was investigated by irradiating the colloidal spheres in solid state with a linearly polarized Ar$^+$ laser beam (488 nm, 130 mW/cm$^2$). For comparison, the colloids were also studied by irradiation with a polarized diode solid state laser beam (532 nm, 130 mW/cm$^2$). Upon the light irradiation, all the colloidal spheres were elongated along the polarization direction of the laser beams. The electron-withdrawing groups showed significant influence on the colloid deformation behavior related with the response to the light irradiation. The colloid deformation was more efficiently induced by irradiation with the laser beams having the intermediate wavelengths between the $\lambda_{max}$ and the absorption band tails of the azo chromophores. When the hydrophilic carboxylic group was used as the electron-withdrawing groups, more significant deformation was induced under the same light irradiation condition, which could be attributed to the higher hydrophilicity of the polymer. Above observations can lead to a better understanding of the photoinduced deformation mechanism of azo polymer colloids.

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## 1. Introduction

Polymers containing aromatic azo chromophores (azo polymers for short) have been intensively investigated in recent years for their photoresponsive properties and potential applications [1–3]. Upon irradiation with UV or visible light at an absorbing wavelength, azobenzene and its derivatives can undergo reversible trans–cis isomerization [4,5]. Triggered by the trans–cis isomerization, azo polymers can show a variety of photoresponsive properties, such as orientation of azo chromophores and associated groups [6], phase transition of liquid crystal polymers [7], thin-film contraction and bending [8–10], and surface-relief-grating (SRG) formation [11]. These photoresponsive properties are determined by both azo chromophore structures and polymeric architecture. Polymers with such properties are promising for applications in data-storage, photo-switching, artificial muscles, and other photonic devices [1–3,10(b)].

Deformation caused by mass-migration at micrometer-level is one of the most fascinating properties observed for azo polymers [2,3]. A well-documented case is surface-relief-grating (SRG) formation on azo polymer films, which clearly demonstrates the light-driven effect [11]. SRGs with sinusoidal profiles can be inscribed on azo polymer films through irradiation with interfering Ar$^+$ laser beams. SRGs are typically inscribed at a temperature well below the glass transition temperature ($T_g$) of the polymers and can be erased by thermal treatment or irradiation with a uniform circularly polarized laser beam. The SRG formation has attracted considerable attention and has been intensively investigated in recent years [12–20]. At the current stage, understanding its mechanism is still a gradual developing process [21,22]. Recently, it has been reported by us that polarized laser beam irradiation can induce significant deformation of azo polymer colloids [23]. The colloidal spheres were prepared by using amphiphilic random azo copolymers and polydispersed azo homopolymers through gradual hydrophobic aggregation [24,25]. Upon irradiation with an Ar$^+$

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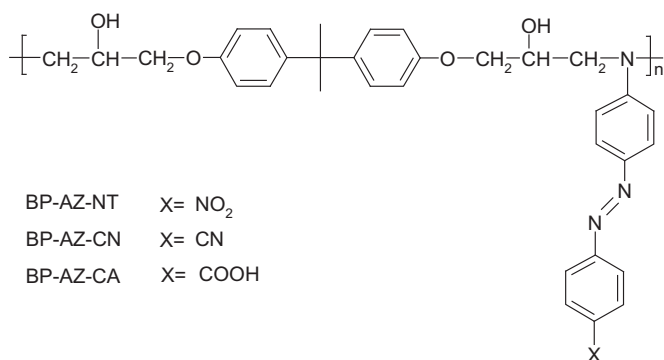E-mail address: wxg-dce@mail.tsinghua.edu.cn (X. Wang).

**Fig. 1.** The chemical structure of BP-AZ-CA, BP-AZ-CN and BP-AZ-NT.



**Fig. 3.** Scattering light intensity as a function of the water content (vol%) in the THF–H$_2$O solutions and dispersions.

laser single beam or interfering beams, the colloidal spheres in solid state can be significantly elongated along the polarization direction of the laser beam [23]. The polymers used for preparing the colloids also show ability to form SRGs upon Ar$^+$ laser irradiation [26]. Some important factors influencing the colloid deformation have been investigated, which include the amounts of azo chromophores in colloids [27], chain architecture [28], composition of the colloids [29], and colloidal size [30].

The correlation between excitation wavelength ($\lambda_{exc}$) and absorption band positions is an important factor to control photochemical or photophysical processes in multiple energy-level systems [5,31]. The azo polymers that exhibit the photoinduced deformation behavior generally contain azo chromophores with a donor-acceptor structure, where the electron-withdrawing groups show important influences on photochemical or photophysical properties. The electron-withdrawing groups can affect both the absorption band position and polarity of the azo chromophores. Some experiments have shown that the SRG formation rates of azo polymers and azo molecular glass are closely related to the electron-withdrawing groups of the functional azo chromophores [26,32,33]. In these cases, the $\lambda_{exc}$ of the irradiation light is fixed at 488 nm, the influence can be attributed to the $\lambda_{max}$ modulation caused by the variation of the electron-withdrawing groups. Recently, SRG formation of azobenzene-derivative polymers has been investigated by irradiation of laser beams with
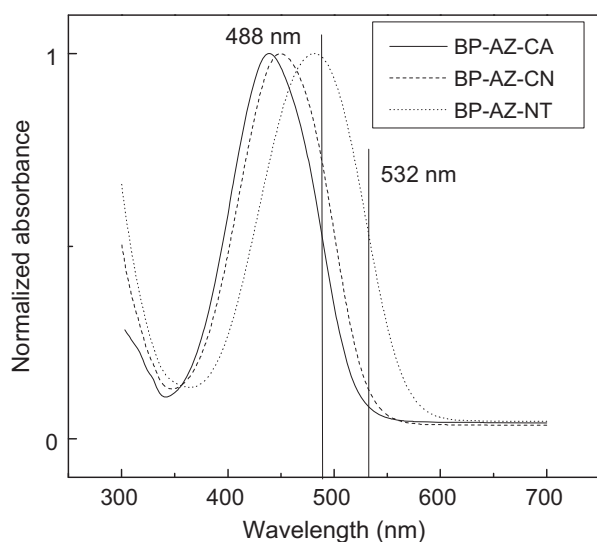
different wavelengths [34]. These observations are important for a better understanding of the mechanism of the SRG formation. For photoinduced deformation of azo polymer colloids, the electron-withdrawing groups of azo chromophores could also play an important role to influence the photoresponsive properties. However, to our knowledge, the influence of this important factor on the photoinduced colloid deformation has not been reported in the literature yet.

In this work, azo polymer colloidal spheres were prepared by using three epoxy-based azo polymers with different electron-withdrawing groups on the azo chromophores. The photoinduced deformation behavior was investigated by irradiating the azo polymer colloidal spheres in solid state with a linearly polarized Ar$^+$ laser (488 nm) beam. For comparison, the colloidal spheres were also studied by irradiation with a polarized diode solid state laser beam (532 nm) under the same conditions. Some important influences of the electron-withdrawing groups on the colloid deformation behavior were observed. The experimental details, results and discussions will be presented in the following sections.

## 2. Experimental section

### 2.1. 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 experiments described below. The chemical structures of the epoxy-based azo polymers (BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT) used to prepare the colloidal spheres are given in Fig. 1. BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT were prepared through azo-coupling reactions between an epoxy-based precursor polymer (BP-AN) and diazonium salts of 4-aminobenzoic acid, 4-aminobenzonitrile, and



**Fig. 2.** UV–vis spectra of BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT in THF solutions. The $\lambda_{exc}$ (488 nm and 532 nm) is indicated with the vertical lines.
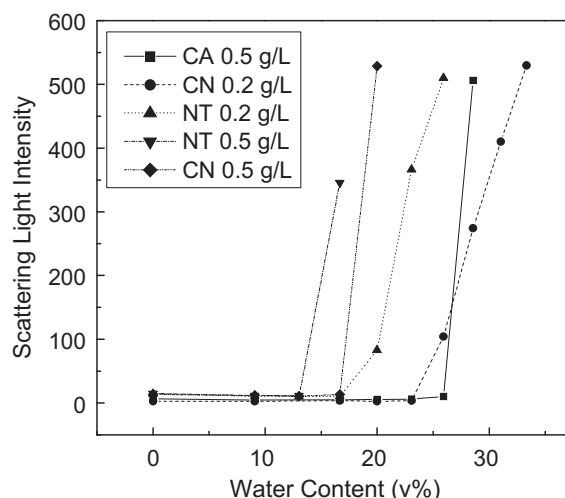
**Table 1**
CWCs of BP-AZ-CA, BP-AZ-CN and BP-AZ-NT in THF–H$_2$O solutions.

|  | BP-AZ-CA | BP-AZ-CN | BP-AZ-CN | BP-AZ-NT | BP-AZ-NT |
|---|---|---|---|---|---|
| $C_{p0}$ (mg/mL)[a] | 0.5 | 0.2 | 0.5 | 0.2 | 0.5 |
| CWC | 26.87% | 23.42% | 20.00% | 19.23% | 16.67% |

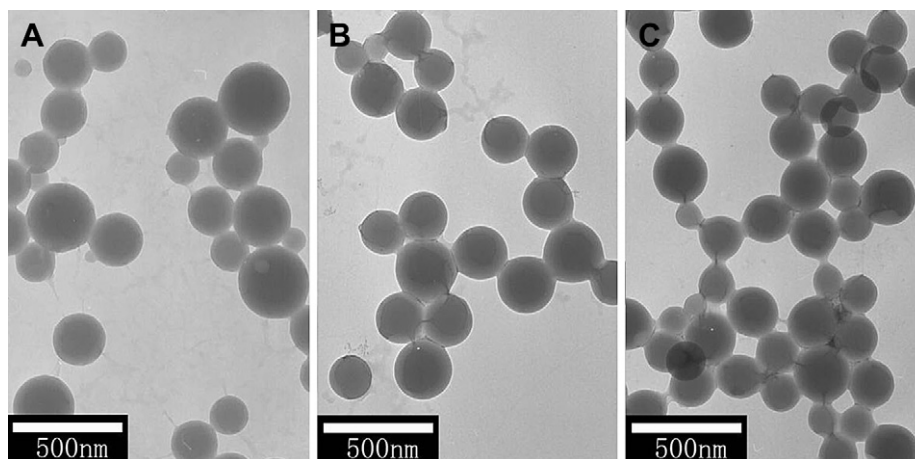[a] $C_{p0}$: the initial polymer concentration in THF solution.

**Fig. 4.** Typical TEM images of the colloidal spheres, (A) BP-AZ-CA, (B) BP-AZ-CN, (C) BP-AZ-NT. The initial polymer concentration and water-adding rate are 0.5 mg/mL, 2 μL/s; 0.2 mg/mL, 5 μL/s; and 0.2 mg/mL, 5 μL/s, respectively.

4-nitroaniline, respectively. The number-averaged molecular weight of the precursor polymer (BP-AN) was 35,000 with a poly-dispersity index of 2.2. The degrees of functionalization (DFs) of the azo polymers were about 100% determined by $^1$H NMR and elemental analysis. BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT are amorphous polymers with glass transition temperatures ($T_g$s) of 160, 132, and 138 °C, respectively. The preparation and characterization have been reported in our previous paper in detail [26].

### 2.2. Colloidal sphere preparation

Suitable amounts of BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT were dissolved in THF to obtain homogeneous solutions with different initial concentrations. The solutions were prepared by stirring at room temperature for 24 h and then putting aside for at least 72 h. The stable colloidal dispersions were obtained by gradually adding deionized water to the THF solutions with a proper rate until the water contents reached 50% (vol%). After that, excess water was added into the dispersions to 'quench' the structures formed in the media. The dispersions were dialyzed against water for 3 days to remove THF before further measurements. The average diameters of the colloidal spheres were controlled by adjusting the initial polymer concentration in THF and water-adding rate in the above processes [27].

### 2.3. Laser irradiation experiment

Linearly polarized beams from an Ar$^+$ laser (488 nm) and a diode solid state laser (532 nm) were used as the light source. The laser beams, after being spatially filtered, expanded and collimated, were adjusted to have the same intensity (130 mW/cm$^2$). The samples used for the light-irradiation experiments were obtained by casting the water suspensions of the colloidal spheres (0.02 mg/mL) on copper TEM grids or silicon wafers. The colloidal spheres were carefully dried under vacuum at 30 °C for 24 h before light irradiation. The colloids were exposed to the linearly polarized laser beam incident perpendicularly to the substrate surfaces for different time periods. All experiments were carried out at room temperature under an air-ambient condition.

### 2.4. Characterization

TEM images of the colloidal spheres were obtained by using a JEOL-JEM-1200EX 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. The samples were observed with the electron microscope before and after the laser light irradiation. No staining treatment was performed for the measurement. SEM measurement was performed on a field emission microscope (JEOL JSM-6301F) with the accelerating voltage of 5 kV. All the samples prepared for SEM studies were coated with thin layers of gold ($\sim$15 nm in thickness). Laser light scattering (LLS) experiments were performed on a commercial LS instrument (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV/LSE-5003) and a solid-state laser (Uniphase, output power = 22 mW, $\lambda$ = 632.8 nm). The average hydrodynamic diameters, which were used to characterize the colloidal sizes, were measured by the dynamic light scattering (DLS). The scattering angle used for the measurement was 90° and the sample temperature was controlled to be 25 °C.

## 3. Results and discussion

The epoxy-based azo polymers (BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT) were used to prepare the colloidal spheres and their chemical structures are given in Fig. 1. The azo polymers, with the difference only in the electron-withdrawing substitutes on the azobenzenes, were prepared through post-polymerization azo-coupling reactions [35]. The conversions of anilino moieties of the precursors were about 100% in the azo-coupling reactions. As the same batch of the precursor polymer was used for the reactions, the degrees of polymerization of the polymers were the same. The synthesis and characterization details of the polymers can be seen in our previous report [26]. Fig. 2 shows the UV−vis spectra of BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT in THF solutions. The spectra of the

**Table 2**
The preparation conditions and the hydrodynamic diameters of the azo polymer colloidal spheres obtained by DLS.

| | $C_{p0}$ (mg/mL)[a] | Water-adding Rate (μL/s) | $D_h$ (nm)[b] | P.I.[c] |
|---|---|---|---|---|
| BP-AZ-CA | 0.5 | 2 | 267 | 0.016 |
| BP-AZ-CN | 0.2 | 5 | 285 | 0.12 |
| BP-AZ-NT | 0.2 | 5 | 294 | 0.057 |

[a] $C_{p0}$: the initial polymer concentration in THF solution.
[b] $D_h$: the hydrodynamic diameter.
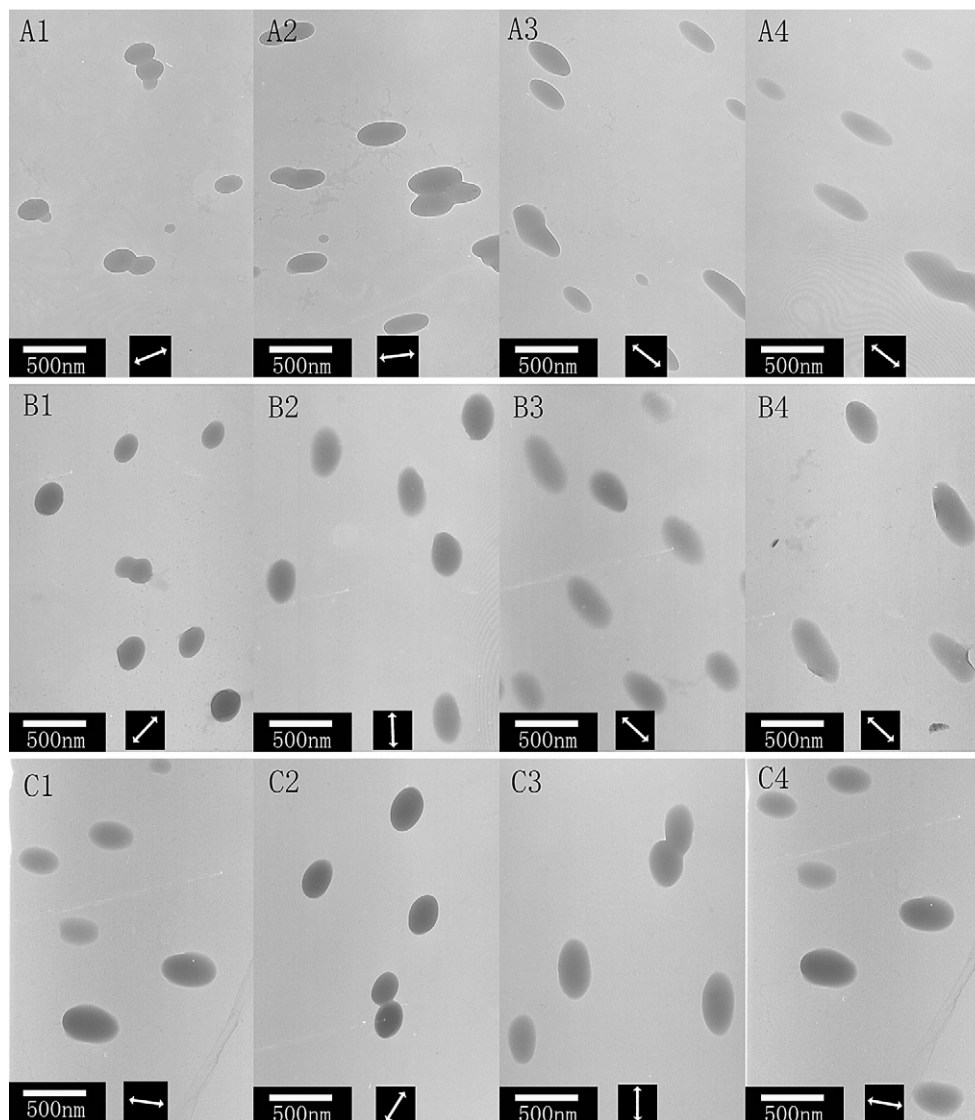[c] The polydispersity index.

**Fig. 5.** Typical TEM images of the colloidal spheres composed of BP-AZ-CA, BP-AZ-CN and BP-AZ-NT after being irradiated with a linearly polarized Ar$^+$ laser beam (488 nm, 130 mW/cm$^2$) for (1) 5 min, (2) 15 min, (3) 30 min, (4) 45 min; for (A) BP-AZ-CA, (B) BP-AZ-CN, (C) BP-AZ-NT.

polymers show typical characteristics of pseudo-stilbene type azo chromophore, where the strong absorbance bands correspond to the π–π* transition [5]. The maximum absorption wavelengths ($\lambda_{\mathrm{max}}$) are 439, 449, and 482 nm for BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT, respectively. The pseudo-stilbene type azo chromophores possess overlapped π–π* and n–π* transition bands both in visible light range. A strong visible light irradiation (such as Ar$^+$ laser irradiation) can induce the chromophores to undergo a rapid trans––cis–trans isomerization cycles [1,3]. The cis-form of the chromophores cannot be detected by ordinary UV–vis spectroscopy due to the short life time [5]. The photoinduced deformation behavior of the colloids is closely related with the absorption band positions, which will be discussed in the following sections in detail.

### 3.1. Colloidal sphere preparation and characterization

The colloidal spheres of BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT were prepared by gradually increasing H$_2$O content in the THF/H$_2$O solutions of the polymers. Fig. 3 shows the plot of the scattered light intensity versus the water content for the BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT solutions. The water contents at the upturning points of the curves are the critical water contents (CWCs), which can be regarded as the points when polymer chains start to aggregate [36]. CWC is an important parameter to characterize the relative hydro-philicity of the polymers, where a larger CWC corresponds to higher hydrophilicity of a polymer. CWC is also correlated with the initial concentration of polymer in the solution and the interaction between the polymeric chains. Table 1 gives the CWCs of these three polymers together with the initial concentrations. The CWCs increase with the decrease of the initial concentrations of the polymers in THF solutions, which is similar to that observed in previous study [24,25]. With the same initial concentration, BP-AZ-CA shows the highest CWC due to the hydrophilic carboxylic groups in the polymer structure. The difference between the CWCs of BP-AZ-CN and BP-AZ-NT could be attributed to the stronger dipo-le–dipole interaction existing in the latter.

Uniform colloidal spheres with similar average diameters were obtained by adjusting the initial polymer concentrations in THF and the water-adding rate. A detailed study concerning the influence of these factors on colloidal size can be seen in our
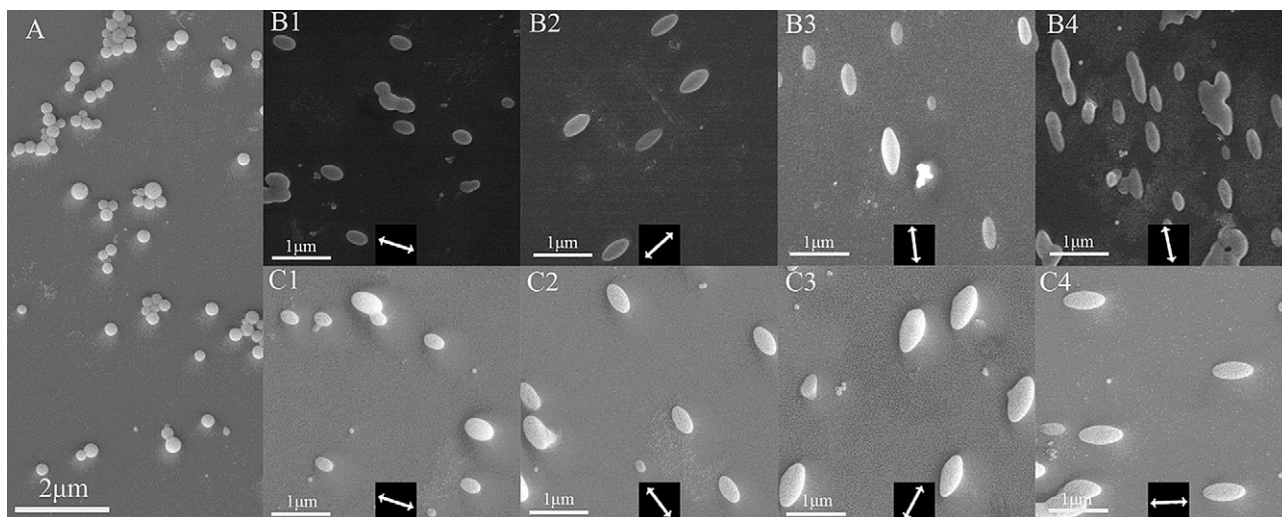
**Fig. 6.** Typical SEM images of the colloidal spheres composed of BP-AZ-CA: (A) before irradiated; (B1−B4) after being irradiated with a linearly polarized Ar$^+$ laser beam (488 nm, 130 mW/cm$^2$) for 5 min, 15 min, 30 min, and 45 min (from left to right); (C1−C4) after being irradiated with a polarized diode solid state laser beam (532 nm, 130 mW/cm$^2$) for 5 min, 15 min, 30 min, and 45 min (from left to right).

previous report [27]. A higher initial concentration is required for BP-AZ-CA to attain colloidal spheres with an average diameter close to those of the other two azo polymers. The colloid sizes and dispersions were characterized by dynamic light scattering (DLS). The solid particles separated from the dispersions were characterized by TEM and SEM. Fig. 4 shows typical TEM images of the colloidal spheres of BP-AZ-CA, BP-AZ-CN, and BP-AZ-NT. The average diameters and the polydispersity index of the colloids were obtained from DLS and are given in Table 2 together with their preparation conditions.

### 3.2. Irradiation with 488 nm light

The "isolated" colloids on the substrates were obtained by casting the diluted water dispersions of the colloidal spheres on copper TEM grids and silicon wafers. The colloidal spheres were carefully dried under vacuum before light irradiation. A linearly polarized beam from Ar$^+$ laser at 488 nm with the intensity of 130 mW/cm$^2$ was used as the light source. The colloidal spheres on the substrates were exposed to the normally-incident laser beam for different time periods under air-ambient condition.
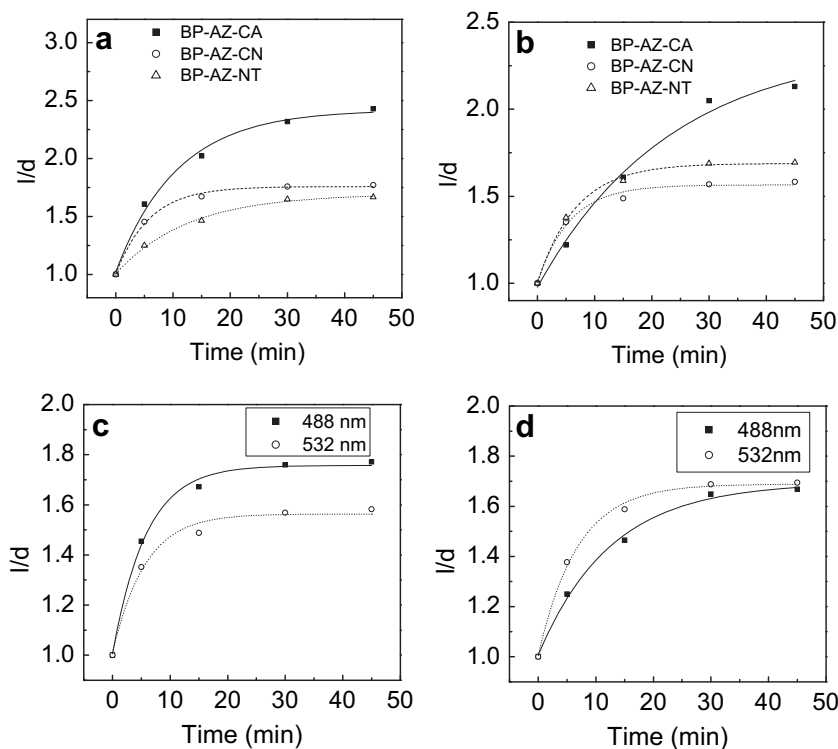


**Fig. 7.** The relationships between the average axial ratios (l/d) of the colloids and irradiation time, (a) irradiated with Ar$^+$ laser beam (488 nm, 130 mW/cm$^2$), (b) irradiated with diode solid state laser beam (532 nm, 130 mW/cm$^2$), (c) BP-AZ-CN colloids, (d) BP-AZ-NT colloids.

Fig. 5 gives typical TEM images of the BP-AZ-CA, BP-AZ-CN and BP-AZ-NT colloids after being irradiated with the laser beam for different time periods. The panels from the top row to bottom row show the colloids of BP-AZ-CA, BP-AZ-CN and BP-AZ-NT. From the left to right of each row, the irradiation time periods are 5, 15, 30, and 45 min. It can be seen that the colloids of all three polymers are significantly elongated especially after irradiated for the longer time. The elongated direction of the colloids is parallel to the polarization direction of the laser beams. Fig. 6 gives typical SEM images obtained from the BP-AZ-CA colloids with average diameters of 267 nm before and after the light irradiation. The pictures in the top row show the deformation after irradiated with the 488 nm laser beam for 5, 15, 30, 45 min. SEM observation confirms the deformation observed by using TEM.

As the colloidal spheres are not monodispersed, the quantitative correlation between laser beam wavelength and deformation degree was obtained through a statistical method. The average axial ratio (l/d) of the colloids (estimated statistically from TEM images of 50 colloidal particles) was used to characterize the deformation of the colloids. Fig. 7(a) gives the relationship between the average axial ratio and irradiation time for the BP-AZ-CA colloids irradiated

with the Ar$^+$ laser beam (488 nm, 130 mW/cm$^2$). The l/d ratios rapidly increase at the first stage and then gradually level off for longer irradiation time. This tendency is the same for the colloids of all three azo polymers. However, the elongation rate at the first stage and the final elongation degree of the colloids are different for the colloids. The colloids of BP-AZ-CA show the faster elongation rate and larger final elongation degree.

### 3.3. Irradiation with 532 nm light

For comparison, the colloids of these three polymers were also irradiation with the linearly polarized laser beam at 532 nm (130 mW/cm$^2$). Fig. 8 gives typical TEM images of the colloids after being irradiated with the 532 nm laser beam for 5, 15, 30, and 45 min, respectively. The pictures in the bottom row of Fig. 6 show the SEM image of BP-AZ-CA colloids after being irradiated with the 532 nm laser beam for 5, 15, 30, 45 min. It can be seen that the colloids of all three polymers are significantly elongated in the polarization direction of the laser beam. The relationship between the average axial ratio and irradiation time for the three type colloids is given in Fig. 7(b), which were also obtained statistically
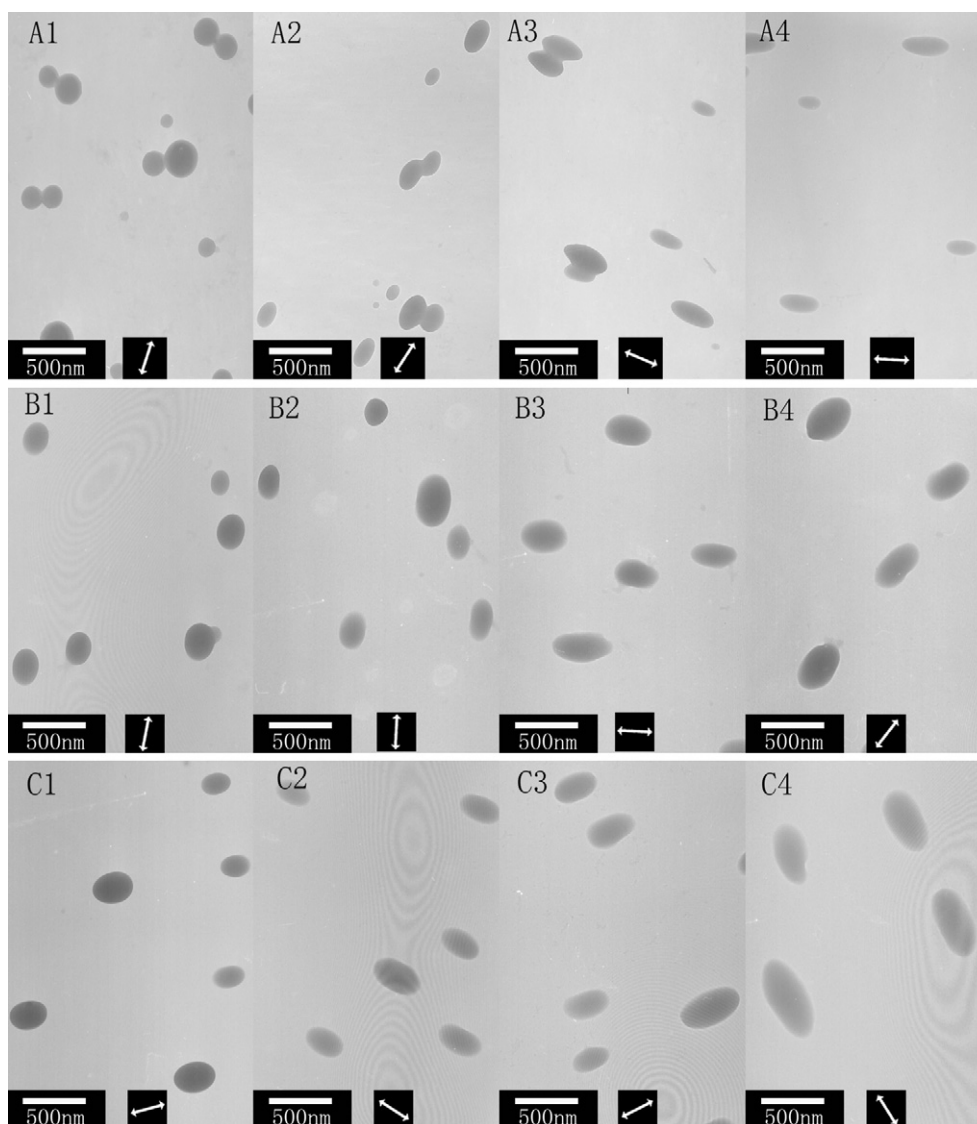


**Fig. 8.** Typical TEM images of the colloidal spheres composed of BP-AZ-CA, BP-AZ-CN and BP-AZ-NT after being irradiated with a polarized diode solid state laser beam (532 nm, 130 mW/cm$^2$) for (1) 5 min, (2) 15 min, (3) 30 min, (4) 45 min; for (A) BP-AZ-CA, (B) BP-AZ-CN, (C) BP-AZ-NT.

as mentioned above. More significant deformation occurs for the colloids composed of BP-AZ-CA than the colloids of the other two polymers. This point is similar to that observed for irradiation with the laser beam at 488 nm.

### 3.4. Influence of electron-withdrawing groups

The electron-withdrawing groups can affect the absorption band position and polarity of the azo chromophores. By comparing the corresponding curves for the BP-AZ-CA colloids in Fig. 7(a) and (b), it can be seen that irradiating with the laser beam at 532 nm causes a slower elongation rate and smaller elongation degree compared with the irradiation at 488 nm. This can be attributed to a weak absorption of BP-AZ-CA at 532 nm (Fig. 2), which is near tail of the absorption band. Above result indicates that the excitation wavelength ($\lambda_{exc}$) plays an important role to influence the colloid deformation process. In order to compare the results of the other two type colloids, the relationship between the average axial ratio and irradiation time for the colloids are re-plotted as Fig. 7(c) and (d) to reveal the wavelength effect. The $\lambda_{max}$ of BP-AZ-CN appears at 449 nm with a red-shift of 10 nm compared with the $\lambda_{max}$ of BP-AZ-CA. The colloids of BP-AZ-CN show a similar dependence on the excitation wavelength as the BP-AZ-CA colloids. BP-AZ-CN colloids also show the slower elongation rate and smaller elongation degree when irradiated with 532 nm laser (Fig. 7(c)). It can also be attributed to the weak absorption of BP-AZ-CN at 532 nm (Fig. 2), which is near the absorption band tail. Comparing with the colloids of above two polymers, BP-AZ-NT colloids show different responsive behavior to these two excitation wavelengths because of the significant red-shift of the $\lambda_{max}$ (482 nm). The excitation light at 488 nm and 532 nm corresponds to the $\lambda_{max}$ and the intermediate point between $\lambda_{max}$ and the absorption band tail, respectively. For the same irradiation time, the colloids irradiated with 532 nm light show a more significant elongation compared with those irradiated with laser beam at 488 nm. The relationship between the average axial ratio and irradiation time for the BP-AZ-NT colloids is given in Fig. 7(d). For the colloids of BP-AZ-NT, particles irradiated with 532 nm light show a larger initial elongation rate compared with that of the colloids irradiated with 488 nm light (in the first 20 min). As the irradiation time increases, the elongation degrees (l/d ratios) gradually reach the saturated values. After being irradiated for 45 min, the elongation degrees of the colloids approach the similar saturated values for the colloids irradiated with the light at the two different wavelengths. This result also indicates that a more efficient colloid deformation can be induced by irradiation with the $\lambda_{exc}$ located at the intermediate wavelength between the $\lambda_{max}$ and absorption band tail.

Above results indicate that electron-withdrawing groups can show significant influence on the colloid deformation behavior through adjusting the absorption band positions of the azo chromophores. By comparing details of the elongation rate and degree of the colloids, another influence of the electron-withdrawing groups can be identified for the azo polymer colloids. It can be seen that the BP-AZ-CA colloids show a much more significant deformation than BP-AZ-CN colloids whether irradiated with the laser light at 488 nm or at 532 nm (Fig. 7). It is interesting to compare this observation with the SRG-forming rates of these two polymers. Upon irradiation with the interfering Ar$^+$ laser beams (488 nm), the SRG-forming rate of a BP-AZ-CA film is very close to that of the BP-AZ-CN film [26]. BP-AZ-CA and BP-AZ-CN have glass transition temperatures ($T_g$s) of 160 and 132 °C, respectively. The higher $T_g$ of the former is due to the hydrogen-bonding between the carboxyl groups. Above results seem to indicate that there is no direct correlation between photoinduced deformation behavior and $T_g$ of the polymers as $T_g$ is more suitable for characterizing bulky

property of the materials. The difference observed on photoinduced deformation behavior of BP-AZ-CA and BP-AZ-CN colloids could be more reasonably attributed to the influence of the electron-withdrawing groups on the colloidal structures. The electron-withdrawing groups of BP-AZ-CA are the hydrophilic carboxylic groups. Therefore, BP-AZ-CA is more hydrophilic than BP-AZ-CN, which can be seen from the CWC data (Fig. 3 and Table 1). The colloidal spheres composed of BP-AZ-CA could be more significantly swollen by aqueous medium during the forming process. After drying, the colloids could possess a less dense core comparing with colloids of BP-AZ-CN and BP-AZ-NT. The colloids with such characteristics will have a lower modulus and show lower resistance to the deformation caused by the light irradiation.

## 4. Conclusion

The current study shows that the electron-withdrawing groups on the azo chromophores have a significant influence on the photoinduced deformation behavior of the azo polymer colloids mainly through its modulation to the absorption band position. The colloid deformation can be more efficiently induced by irradiation with the laser beams at the intermediate wavelengths between the $\lambda_{max}$ and the absorption band tails of the azo chromophores. Furthermore, the electron-withdrawing groups can also affect the photoinduced deformation behavior through its influence on hydrophilicity of the polymers.

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