

Temperature dependence of localised surface plasmon resonance effect on photoisomerisation of azobenzene units in Ag/poly(N-isopropylacrylamide)-block-poly{6-[4-(4-methylphenyl-azo)phenoxy] hexylacrylate} composite particles

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A series of Ag/poly(N-isopropylacrylamide)-block-poly{6-[4-(4-methylphenyl-azo)phenoxy] hexylacrylate} (PNIPAM-b-PAzoM) composite particles (CPAs) with varying concentrations of Ag nanoparticles are prepared by self-assembly of PNIPAM-b-PAzoM in a mixture of H₂O and THF at first, and then by chemical reduction of AgNO₃ in the suspension of the self-assembled particles. The distance between Ag nanoparticles and azobenzene units is determined by the concentration of Ag nanoparticles and temperature because hydrophilic poly(N-isopropylacrylamide) (PNIPAM) chains are thermosensitive and adsorbed with Ag nanoparticles. Both *trans*-to-*cis* and *cis*-to-*trans* photoisomerisations of the CPAs are investigated at different temperatures and concentrations of Ag nanoparticles. Experimental results reveal that, at room temperature, both rates of the *trans*-to-*cis* and the *cis*-to-*trans* photoisomerisations are decreased by the localised surface plasmon resonance of Ag nanoparticles with experimental concentrations lower than 0.04 mmol/l. With the temperature increasing and gradually closing to the low critical solution temperature of PNIPAM chains the rate of the *trans*-to-*cis* photoisomerisation can be found to be enhanced gradually within the same concentration range of Ag nanoparticles. However, the rate of the *cis*-to-*trans* photoisomerisation is little affected. Detailed analysis shows that this effect is related to the overlap of azobenzene absorption and Ag nanoparticle absorption.

1. Introduction: In recent years, Ag, Au and other metal nanoparticles have been widely investigated because of their unique features in optical [1] sensing [2–4] and information storage [5], from which it is well established that light at the surface plasmon resonance frequency interacts strongly with metal particles and excites a collective electron motion or plasmon [6]. As a result, the local electromagnetic field in the vicinity of the metallic particles can be enhanced by several orders of magnitude and is defined as the localised surface plasmon resonance (LSPR) [7]. The LSPR of the nanoparticles is strongly affected by many parameters, such as morphology, size, composition and interparticle spacing as well as the local environment of the nanoparticles [8, 9]. On the other hand, the LSPR of the nanoparticles can enhance light actions, including chemical or physical interactions and has been applied in so many areas that special attention in polymer researches is undoubtedly paid to polymer nanocomposites that are promising substances for all of the mentioned areas and many others [10, 11]. For photo-sensitive liquid crystalline polymer (LCP) such as LCPs containing azobenzene moieties, when nanocomposites are formed with noble metal nanoparticles, interactions between light and the nanocomposite polymers involve two aspects: one is the photo-induced orientation of LCPs [12–14] and the other relates to the interactions between light and noble metal nanoparticles [15, 16]. The above two kinds of interactions can cooperate with each other by making use of the plasma enhancement. In one previous work, it is demonstrated that LSPR of Ag nanoparticles can enhance the rate of photo-induced orientation of azobenzene-containing polymers (azopolymers for short) in Ag-doped azopolymer thin films [17].

In the work reported in this letter, a new Ag/azopolymer CPA has been designed to study the distance dependence of Ag nanoparticles'

LSPR effect on the photoisomerisation process of azobenzene. The CPA is composed of amphiphilic diblock copolymers poly(N-isopropylacrylamide)-block-poly{6-[4-(4-methylphenyl-azo)phenoxy] hexylacrylate} (PNIPAM-b-PAzoM) and Ag nanoparticles, in which Ag nanoparticles are selectively adsorbed on the poly(N-isopropylacrylamide) (PNIPAM) block by chemical reduction of Ag⁺ in the presence of PNIPAM-b-PAzoM aggregates. In this way, the distance between Ag nanoparticles incorporated within the PNIPAM block and azobenzene groups can be monitored by temperature changing because of the thermosensitivity of PNIPAM, which enables us to reveal the distance dependence of the LSPR effect on the photoisomerisation of azobenzene groups in Ag/polymer composites although changing of temperature.

2. Experimental section

2.1. Synthesis of PNIPAM-b-PAzoM block copolymers: PNIPAM-b-PAzoM (the structure is shown in Fig. 1a) is synthesised and characterised by similar methods to those reported in our previous work [18], during which the molecular weight and molecular weight distribution for each chain segment in the copolymer are controlled by successive reversible addition-fragmentation chain transfer (RAFT) polymerisation. A THF solution of NIPAM (4.52 g, 40 mmol), AIBN (13 mg, 0.08 mmol) and CPDB (0.177 g, 0.8 mmol) in a glass tube was degassed by three freeze-pump-thaw cycles, sealed off under vacuum and then heated at 70°C for 24 h. PNIPAM-SC(S)Ph was isolated after dissolving in THF and precipitation in diethyl ether three times. The polymer had 90 repeating units, according to the NMR spectrum, and was used as a macro-RAFT agent to polymerise the azobenzene monomer. A mixture of azobenzene monomer (0.27 g, 0.74 mmol), PNIPAM-CPDB (0.138 g, 0.0185 mol) and AIBN (0.6 mg, 0.0037 mmol) was dissolved in 6

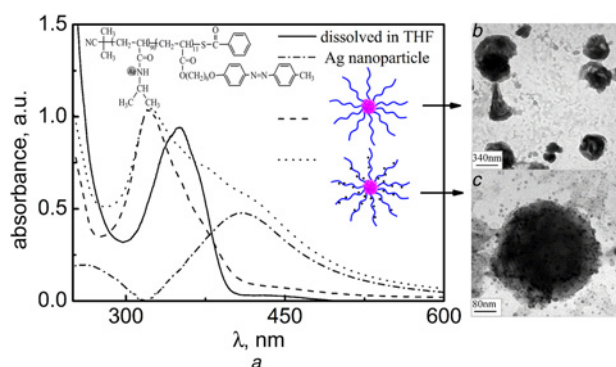


Figure 1 Fig. 1a: chemical structure of PNIPAM-b-PAzoM (m : 90 and n : 11), absorption spectra of PNIPAM-b-PAzoM in various states (dashed line, dissolved in THF; hyphenated line, CP; dotted line, CPA and dash dotted line, Ag nanoparticle), the model of CP and CPA (Blue: PNIPAM, Pink: PAzoM). Figs. 1b and c: typical TEM images of CP and CPA, respectively

ml of THF. The mixture solution was treated by the same degassing process mentioned above; the resulting solution was then heated to 80°C for 48 h. Afterwards, the reaction mixture was dissolved in THF and precipitated in diethyl ether three times. The number of repeat units in the poly{6-[4-(4-methylphenyl-azo)phenoxy]hexylacrylate} (PAzoM) block was estimated to be 11 by quantitative analysis according to the NMR spectrum.

2.2. Preparation of CPAs composed of copolymer particles (CPs)/Ag nanoparticles (CPA): Self-assembly of the copolymer was conducted according to the procedure reported in the literature [19]. PNIPAM-b-PAzoM was dissolved in THF to obtain a solution with a concentration of 3 mg/ml. Milli-Q water was added into the stirred THF solution at a rate of 5 μ l/s. After the water content reached 66.7 vol%, the stirring was continued for an additional 2 h, and the suspension containing CPs was dialysed against water for 72 h to remove the THF.

The preparation of CPA was carried out by the chemical reduction of AgNO_3 with NaBH_4 in the suspension according to the method reported in the literature [20]. To obtain the CPAs, 0.10 ml of AgNO_3 (0.001 M) solution was added to 3 ml CP and the mixture was stirred for 30 min under N_2 . Thereafter, 0.1 ml of aqueous solution of NaBH_4 (0.01 M) was quickly added to the solution under stirring for 4 h.

The average molecular weight and molecular weight distribution of the copolymers were measured using gel permeation chromatography (GPC), which are $M_n = 2.45 \times 10^4$, $M_w/M_n = 1.15$ for PNIPAM and $M_n = 2.71 \times 10^4$, $M_w/M_n = 1.19$ for PNIPAM-b-PAzoM, respectively.

2.3. Measurements: Molecular weights and molecular weight distributions were determined by GPC using a linear Styragel column at an oven temperature of 50°C. The Waters 1515 pump and a Waters 2414 differential refractive index detector (set at 40°C) were used. The eluent was THF at a flow rate of 1.0 ml/min. UV-vis absorption spectra were measured on an SHIMADZU UV-2550 PC spectrophotometer. Observation of Ag nanoparticles was carried out by a JEOL-2010 transmission electron microscope (TEM). Photoisomerisation of azo chromophores was induced by a high-pressure mercury arc combined with a UV filter. The intensity of the UV light (~ 365 nm) was about 2.1 mW cm^{-2} .

3. Results and discussion

3.1. Characterisation of CPA: From data of molecular weights it can be seen that there is a relatively long chain of PNIPAM in the copolymer compared with the chain of PAzoM. Under this

circumstance, aggregates self-assembled in THF/Milli-Q water from these amphiphilic copolymers will have a hydrophobic PAzoM core with a long hydrophilic PNIPAM chain corona. The model of such aggregates is shown in Fig. 1a.

In the TEM photograph of the CP (Fig. 1b), the dark area indicates the PAzoM core, whereas the light area around the dark core is the PNIPAM chains. From the scale bar and gradient colour changing shown in the photograph, it is easily deduced that the sphere is made up of some aggregates. From the TEM photograph of the CPA (Fig. 1c), Ag nanoparticles can be clearly observed and are distributed along the PNIPAM chains, in which Ag nanoparticles are small black dots with a diameter of less than 10 nm. This result comes from a strong localisation of the Ag^+ ions formed by complexation between Ag^+ ions and nitrogen atoms in PNIPAM chains before the reduction reaction. It is noteworthy that, from this model, the distance between azobenzene units and Ag nanoparticles are determined by PNIPAM chain distribution because Ag nanoparticles are immobilised by the polar groups on the PNIPAM chain. The distance would decrease as soon as the collapse of the PNIPAM chains takes place with increase of temperature.

3.2. Photoisomerisation of azobenzene units in self-assembly aggregates of PNIPAM-b-PAzoM: The absorption spectra of PNIPAM-b-PAzoM in THF solution and in the self-assembly aggregates, which has been dialysed against water for 72 h to remove THF, in Milli-Q water are shown in Fig. 1a. The main absorption of two samples are located at 352 and 320 nm, respectively, both of which are related to the $\pi-\pi^*$ electronic transitions of the azobenzene *trans*-isomers. A blue-shift of 32 nm (from 352 to 320 nm) suggests that the azobenzene units form H-aggregation within the self-assembly aggregates [21]. On the other hand, there is still a little shoulder peak at 450 nm corresponding to the $n-\pi^*$ electronic transition of the *cis*-isomers for both of them.

It is well known that azobenzene units can undergo a *trans*-to-*cis* isomerisation under UV irradiation and a *cis*-to-*trans* isomerisation under visible light irradiation. Irradiation at room temperature (23°C) with light at 365 nm from the high-pressure mercury lamp (obtained through a filter) was used to induce the *trans*-to-*cis* isomerisation, then with light at 436 nm to induce *cis*-to-*trans* isomerisation of self-assembly aggregates. The irradiation process was traced by UV-vis spectroscopy measurements as shown in Fig. 2. The results in Fig. 2a show that under the irradiation at 365 nm the strength of the absorbance at 320 nm gradually decreases while the absorption strength at 440 nm increases (*cis* $n-\pi^*$ transition). This change is a typical characteristic of the *trans*-to-*cis* isomerisation of the azobenzene units (Fig. 2a). From the inset of Fig. 2a, it can be seen that there is no sensible red shift of the absorption during irradiation at 365 nm, showing the disaggregation of H-aggregation takes place in the same time scale as the *trans*-to-*cis* isomerisation, both being quicker than the absorption measurement. This result is different from the behaviour of the self-assembly aggregates composed of PAA-b-PAzoM that shows a sensible red shift during irradiation of light at 350 nm [18]. The strong hydrophilic character of PAA chains makes the disaggregation of H-aggregation slower than the *trans*-to-*cis* isomerisation of azobenzene units.

From this analysis, a slow aggregation of azobenzene units could be expected for the *cis*-to-*trans* isomerisation process. In Fig. 2b, it can be seen that under visible light irradiation, a sensible shift of the maximum absorption takes place along with the irradiation time. The entire process can be divided into three stages with respect to the shift of the maximum absorption band (inset in Fig. 2b). First, the maximum absorption peak at 313 nm gradually shifts to 342 nm, and the absorption strength increases at the same time. During this period, there is no formation of H-aggregations and the *cis*-to-*trans* isomerisation of the azobenzene units takes place.

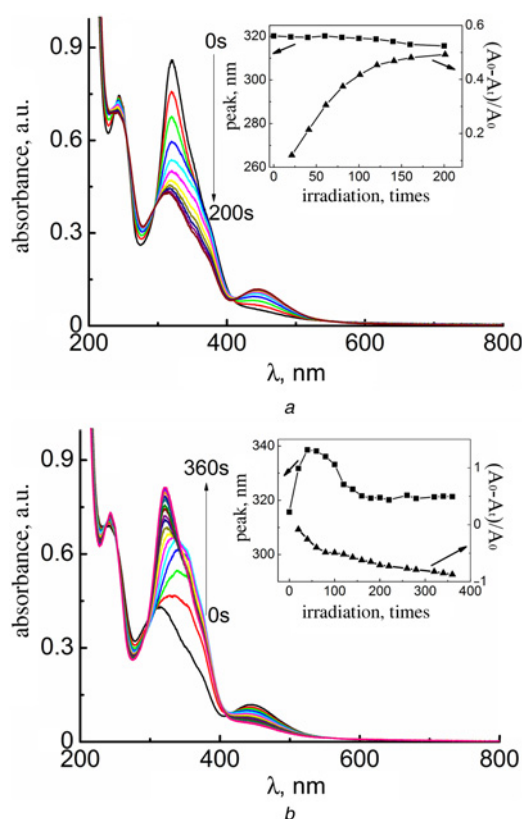


Figure 2 UV-vis spectra of PNIPAM-b-PAzoM in self-assembly particles under irradiation: at 365 nm (Fig. 2a) and at 436 nm (Fig. 2b) for different times, $\Delta t = 20$ s
 Insets: Changing of wavelength and absorption strength at the main absorption along with the irradiation time

The shift is caused by the increase of *trans* isomers. Secondly, along with the increasing of absorption strength of $\pi-\pi^*$ transition, the maximum absorption wavelength gradually shifted from 342 to 320 nm, showing H-aggregation is formed. Thirdly, the strength of the absorbance at 320 nm gradually increases, but the shift of absorption wavelength, showing the formation of large amounts of the H-aggregation has been completed before this time, small amount of *trans* isomers do not aggregate further. This process is identical with the earlier observation [18].

3.3. Photoisomerisation of azobenzene units in CPA: For CPA, the same experiment on the photoisomerisation of azobenzene units was also performed as that for PNIPAM-b-PAzoM aggregates. However, we found that the concentration of Ag nanoparticles affected the photoisomerisation behaviour of azobenzene groups in Ag/PNIPAM-b-PAzoM CPAs.

Fig. 3 gives the relationship between the concentration of Ag nanoparticles and first-order rate constant k_{tc} for the *trans*-to-*cis* and k_{ct} for the *cis*-to-*trans* photoisomerisation of azobenzene units in CPA. The rate constant k of the photoisomerisation of azobenzene units, for *trans*-to-*cis* and *cis*-to-*trans*, can be defined according to absorption (at $\lambda_{\max}$) against the irradiation time, which has the following formula expression [22]:

$$\ln[(A_{\infty} - A_t)/(A_{\infty} - A_0)] = -kt \quad (1)$$

where A_t , A_0 , and A_{∞} are the absorbances at $\lambda_{\max}$ (320 nm for *trans* $\pi-\pi^*$ transition) at time t , time zero and infinite time, respectively. The first-order kinetic plot for the *trans*-to-*cis* photoisomerisation of PNIPAM-b-PAzoM self-assembly is shown in the inset in Fig. 3a for comparison, from which the value of k_{tc} with no Ag can be

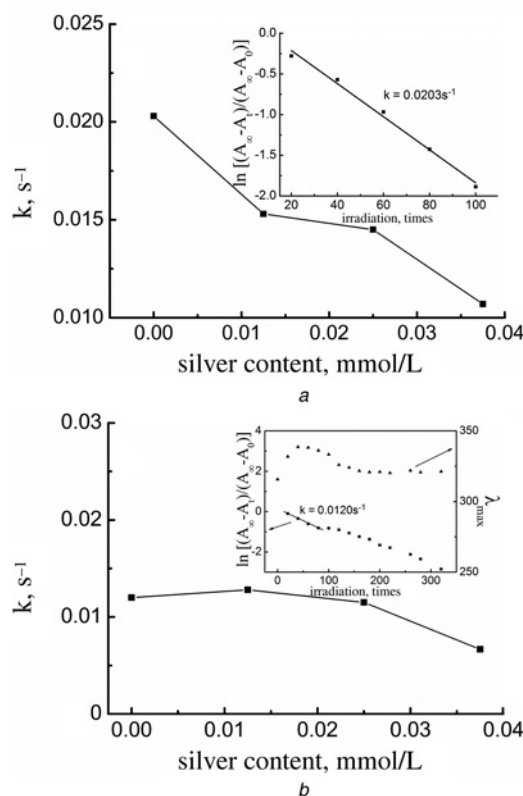


Figure 3 Relationship between the concentration of Ag and first-order rate constant: k_{tc} (Fig. 3a) and k_{ct} (Fig. 3b) of azobenzene units in CPA
 Insets: Dependence of $\ln [(A_{\infty} - A_t)/(A_{\infty} - A_0)]$ on irradiation time at 320 nm for *trans*-to-*cis* (Fig. 3a) and for *cis*-to-*trans* (Fig. 3b) isomerisation

obtained. Similar treatments have also been performed for CPAs, and the obtained values for different Ag content are also shown in Fig. 3a. For the *cis*-to-*trans* photoisomerisation, the value of k_{ct} can be obtained by using absorptions at $\lambda_{\max} = 320$ nm, and the results are shown in Fig. 3b.

From the results shown in Fig. 3, it can be seen that the value of k is decreased along with the increasing of Ag content, both for *trans*-to-*cis* and *cis*-to-*trans* photoisomerisations. Particularly, compared with samples with various Ag content, the value of k_{tc} for the sample without Ag particles is the maximum value, although it is known from Fig. 1 that the Ag nanoparticle has absorption at $\lambda_{\max} = 410$ nm (including 365 and 436 nm for absorptions of *trans* and *cis* azobenzene groups, respectively) that would result in the LSPR effect of Ag nanoparticles. This result is way beyond our expectation that along with the increasing of the concentration of Ag nanoparticles, the LSPR effect should be enhanced as the average distance between Ag nanoparticles and azobenzene groups and the total intensity of the LSPR increase. A possible reason for this phenomenon lies in the absorption overlap of two absorptions of Ag nanoparticles and azobenzene groups, resulting in sharing irradiation energy by two components. To make this clear, it is necessary to keep the concentration of Ag nanoparticles and change the average distance between Ag nanoparticles and azobenzene groups at the same time. The sole dependence of the photoisomerisation on the distance between azobenzene units and Ag nanoparticles will be presented in the next sub-Section.

On comparing Fig. 3a with Fig. 3b, little difference can be found for the two kinds of isomerisations. With the increase of Ag content, the values of k_{ct} decrease slightly. The result can also be explained by sharing irradiation energy as given below. The absorption region of Ag nanoparticles is at about 410 nm. When the Ag-embedded samples are irradiated by UV or visible light, Ag nanoparticles absorb a portion of light and as a result azobenzene units absorb

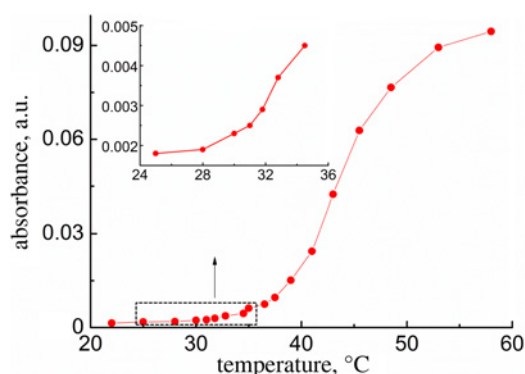


Figure 4 Relationship between temperature and absorbance of CP at 600 nm

Heating rate of 0.2 K/min

Inset: Magnified view of the curve within 25–35°C.

less than that of the unembedded samples. On the other hand, the *cis*-isomer is of a higher inner-energy than *trans*-isomer [14], and the transition from *cis*-to-*trans* can take place spontaneously. Thus, the LSPR would not influence photoisomerisation of *cis*-to-*trans* too much.

3.4. Dependence of photoisomerisation on the distance between azobenzene units and Ag nanoparticles in Ag/PNIPAM-*b*-PAzoM CPAs: It is known that when suspending in water under room temperature, PNIPAM chains in CPAs are thermally sensitive with a low critical solution temperature (LCST) [23]. In this work, PNIPAM chains around the azobenzene units undergo a hydrophilic to hydrophobic transition with a dramatic volume decrease at around the LCST (39°C). As shown in Fig. 4, the absorbance of the suspending solution of CPAs at 600 nm increases with increasing temperature, and at 38°C a dramatic increase in absorption can be observed, suggesting that the PNIPAM chains are shrunk. In Fig. 4, from 32 to 35°C, an increase in absorption can be observed; it is easily deduced that the PNIPAM has already shrunk within this temperature range. In this way, it can be expected that the distance between Ag nanoparticles and azobenzene units will be shortened along with the shrinking of PNIPAM chains, and the following discussion about dependence of the photoisomerisation rate on distance between Ag nanoparticles and azobenzene units will be limited to below 35°C.

At three different temperatures, 20, 25 and 35°C, the photoisomerisation of azobenzene units in CPAs were studied by the same procedure described in sub-Section 3.3. The values of k_{ic} at different temperatures were obtained and compared with each other, see Fig. 5. As shown in Fig. 5a, with the increase of temperature, k_{ic} values increase. If the increase of k_{ic} for no Ag CPAs is caused by the increase in temperature, the increase for the Ag containing samples must be caused partly by the LSPR effect. It is well known that, when temperature increases, PNIPAM chains will shrink, resulting in a decrease of the distance between Ag nanoparticles and azobenzene units, which will enhance the light action called the LSPR effect [7, 9]. On the other hand, from the present results shown in Fig. 5, the k_{ic} value of the sample with an Ag concentration of 0.013 mmol/l increases most, which also shows a possibility that the maximum enhancement would exist at a certain concentration of Ag nanoparticles.

A different situation can be found for k_{ct} values in Fig. 5b, in which k_{ct} shows little change along with increasing of temperature, irrespective of the Ag content. More obviously, with increasing of Ag content, k_{ct} is decreasing, rather than increasing. For a deeper understanding of this phenomenon, an experiment for a solution of the copolymer in DMF was designed and performed for the

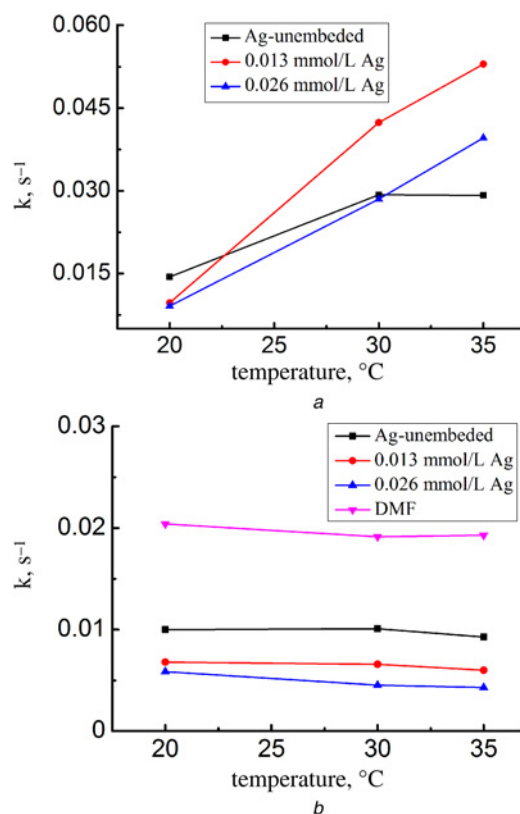


Figure 5 Temperature dependence of the first-order rate constant: k_{ic} (Fig. 5a) and k_{ct} (Fig. 5b) of azobenzene units in CPA

cis-to-*trans* isomerisation. As shown in Fig. 5b, the rate of *cis*-to-*trans* isomerisation in solution is larger than that in CPAs and k values at different temperatures have the same changing tendency as the CPAs. Two points can be summarised by comparison of the results: one is that there is no positive dependence of *cis*-to-*trans* isomerisation on temperature, and the second is that the distance between azobenzene units and Ag particles has little effect on the k_{ct} values of photoinduced *cis*-to-*trans* isomerisation at 436 nm. Contrary to *trans*-to-*cis* isomerisation, along with increasing of Ag content, k_{ct} values are decreased, as shown in Fig. 5b; this is mainly caused by the weak absorption of *cis*-azobenzene units and the relatively strong absorption of Ag particles at the same wavelength of 436 nm in CPAs. From these results, it can be deduced that the enhancement in the rate of the photo-induced alignment of composite Ag/LCP is obtained by enhancing the rate of the *trans*-to-*cis* photoisomerisation, other than the *cis*-to-*trans* photoisomerisation as the whole photo-induced alignment process comes from these two photochemical reactions.

4. Conclusion: In summary, a series of Ag/ PNIPAM-*b*-PAzoM CPAs has been prepared to investigate the effects of Ag nanoparticles' LSPR on photoisomerisation of azobenzene units, in which PNIPAM-*b*-PAzoM is an amphiphilic diblock copolymer, containing thermosensitive PNIPAM chains as the hydrophilic block. From the experiment on photoisomerisation of azobenzene units in CPA with different concentrations of Ag nanoparticles, it is found that the rates of the *trans*-to-*cis* and the *cis*-to-*trans* photoisomerisation are decreased with increasing concentration of Ag nanoparticles. Keeping the concentration constant, the sole distance dependence of both rates have been investigated by monitoring the temperature of Ag/ PNIPAM-*b*-PAzoM CPAs. Results from experiments at different temperatures show that the rate of photo-induced *trans*-to-*cis* isomerisation can be enhanced by adding Ag nanoparticles, and

the LSPR effect can be enhanced by shortening the distance between Ag nanoparticles and azobenzene groups. Contrarily, there is no sensible change in the rate of the *cis*-to-*trans* photoisomerisation at a given temperature; low absorption of *cis* isomers and total overlap with absorption of Ag nanoparticles are responsible for this result.

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6 References

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