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PAPER

Preparation of polymer single chain nanoparticles using intramolecular photodimerization of coumarin

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We present a new and easy method for preparing polymer single chain nanoparticles (SCNPs). It uses the photodimerization of coumarin groups located on the same chain to obtain the intrachain cross-linking required for chain collapse in solution. To demonstrate the approach, samples of a random copolymer composed of *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and 4-methyl-[7-(methacryloyl)oxy-ethyl-oxy]coumarin (CMA), with 7 or 13 mol% of CMA, were synthesized *via* the reversible addition–fragmentation chain transfer (RAFT) polymerization. We show that well-defined SCNPs could be obtained by the intrachain photodimerization of coumarin groups upon $\lambda > 310$ nm UV irradiation in a dilute copolymer solution. The coil-to-globule transition induced by intrachain photo-cross-linking was investigated by means of ¹H NMR spin–spin relaxation time (T_2). The result indicates that the photoinduced chain collapse is accompanied by a sharp increase of the fraction of chain segments having reduced mobility. SCNPs were further used as a nanoreactor to synthesize gold nanoparticles (AuNPs) *in situ*. In tetrahydrofuran, the rate of AuNP formation was found to be dependent on the polymer chain conformation and mobility determined by the dimerization degree of coumarin. This provides a means to optically control the kinetics of AuNP formation.

1. Introduction

In recent years, polymer nanoparticles have attracted much attention in the field of nanoscience and nanotechnology due to their facile preparation and potential applications in many areas such as drug delivery systems and microelectronics.^{1–5} A number of approaches, including emulsion polymerizations and block copolymer (BCP) self-assembly, have been developed to fabricate polymer nanoparticles.^{6–12} To obtain ultra-fine nanoparticles with size below 20 nm, the strategy of using intramolecular (intrachain) cross-linking to induce the coil-to-globule transition and polymer chain collapse, resulting in the so-called single chain nanoparticles (SCNPs), has gained increasing interest. By using various chemical and physical cross-linking methods, well-defined polymer SCNPs were prepared through single chain collapse in dilute polymer concentration that prevents the intermolecular (interchain) cross-linking from happening.^{13–20}

Coumarin and its derivatives have been widely utilized in designing photosensitive polymeric materials.²¹ Recently, our group has exploited the use of reversible photodimerization of

coumarin to prepare reversibly photo-cross-linkable BCP micelles, vesicles, nanogels and other photoresponsive polymer nanoparticles.^{22–26} Herein, we demonstrate that making use of the reversible photodimerization reaction of the chromophore as shown in Fig. 1, intrachain photo-cross-linking of coumarin-containing polymers provides a facile means of producing SCNPs. By dissolving coumarin-containing polymers in a good solvent at a very low concentration, the photo-cross-linking through a photoinduced cycloaddition reaction under $\lambda > 310$ nm irradiation can be controlled to occur intramolecularly, leading to the collapse of single chains and the formation of SCNPs. Furthermore, intrachain de-cross-linking could be obtained upon UV irradiation at $\lambda < 260$ nm. In order to get insight into the coil-to-globule transition associated with chain collapse in solution, we carried out an investigation using ¹H NMR spin–spin relaxation time (T_2) and found evidence that the conformational transition is accompanied by a sharp increase in the fraction of chain segments having reduced mobility. Moreover, by using the coumarin-containing polymer shown in Fig. 1, the resulting SCNPs could be further utilized as nanoreactors to synthesize gold nanoparticles (AuNPs) *in situ*. We found that in tetrahydrofuran (THF) the kinetics of AuNP formation is sensitive to the polymer chain conformation and mobility that are determined by the photodimerization degree of coumarin groups.

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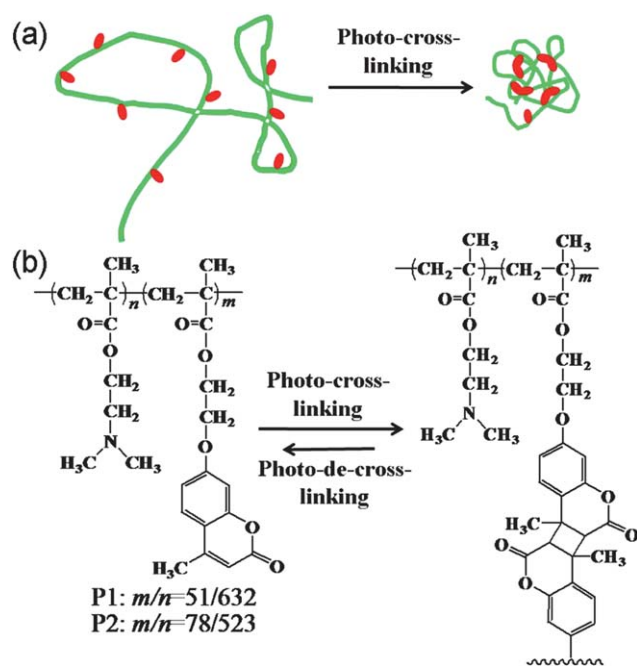


Fig. 1 (a) Schematic illustration of preparation of polymer SCNPs through intrachain photo-cross-linking. (b) Chemical structures of coumarin-containing random copolymers of P(DMAEMA-co-CMA) and the reversible photo-cross-linking reaction activated by UV light at two different wavelengths.

2. Experimental

2.1 Materials

All chemicals were purchased from Aldrich and used as received unless otherwise noted. *N,N*-Dimethylaminoethyl methacrylate (DMAEMA, 98%) was passed through a basic aluminium oxide column and distilled under vacuum prior to use. 4-Methyl-[7-(methacryloyl)oxy-ethyl-oxy]coumarin (coumarin methacrylate, CMA) was synthesized by using a previously reported method.²² 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. The chain transfer agent (CTA), 2-(2-cyano-propyl) dithiobenzoate (CPDB), was synthesized according to a literature method.²⁷

2.2 Synthesis of coumarin-containing polymer

The general conditions for RAFT polymerization were the same as in our previous reports.²⁵ Using the sample P2 in Fig. 1 as example, the synthetic procedure is as follows. DMAEMA (1.55 g, 10 mmol), CMA (432 mg, 1.5 mmol), CPDB (2.2 mg, 10 μ mol) and AIBN (0.4 mg, 2.5 μ mol) were dissolved in 4 mL anisole (99%, anhydrous) in a 10 mL flask. The reaction mixture was degassed under vacuum and refilled with nitrogen for 10 min. Then, the flask was placed in a pre-heated oil bath at 65 °C for 24 h. After polymerization, the reaction mixture was cooled to room temperature; the polymer was collected after three times of precipitation in hexane, and dried under vacuum for 24 h. The obtained polymer has a number-average molecular weight $M_n = 103\,700\text{ g mol}^{-1}$ and a polydispersity index PDI (M_w/M_n) = 1.15 according to SEC measurements using polystyrene (PS) standards. From the ¹H NMR spectrum (in CDCl₃), the units of

DMAEMA and CMA were estimated to be 523 and 78, respectively (the composition determination used the resonance signals of the side methylene groups of CMA and DMAEMA at 4.3 and 4.0 ppm, respectively).

2.3 Preparation of single chain nanoparticles

100 mg of the copolymer was dissolved in 100 mL of THF or *d*-chloroform (CDCl₃, for NMR measurement) and stirred overnight. After being filtered with a 200 nm pore size Teflon filter, the solution was then exposed to UV light $\lambda > 310\text{ nm}$ (intensity $\approx 900\text{ mW cm}^{-2}$). The dimerization degree (DD) of coumarin was monitored by UV-vis spectra and calculated according to $DD = 1 - A_t/A_0$, where A_0 and A_t are the initial absorbance and the absorbance after irradiation time t at 320 nm, respectively. After the dimerization reached the maximum value ($>70\%$), the chain cross-linking reaction was considered to be completed; the solution could be concentrated under vacuum distillation and polymer nanoparticles precipitated in hexane were then dried under vacuum overnight. Nanoparticles can be re-dispersed in THF or CHCl₃ to form a homogenous solution with a desired concentration.

2.4 Synthesis of gold nanoparticles *in situ*

The synthesis of AuNPs was conducted in both THF and water solution with the presence of polymer nanoparticles.²⁸ Here, using the reduction reaction in water as example, details are as follows. P2 in a THF solution (1 mg mL⁻¹) was fully cross-linked under $\lambda > 310\text{ nm}$ UV light. The polymer solution was then dialysed against water for 24 h to fully exchange the solvent. The aqueous solution was filtered with a 200 nm pore size filter and diluted to 0.5 mg mL⁻¹. By adding HAuCl₄ (47 μ g, 0.12 μ mol) aqueous solution to 0.5 mL of P2 nanoparticle solution, the reduction reaction was carried out under stirring at room temperature and followed by UV-vis spectroscopy.

2.5 NMR measurements of nanoparticles

The ¹H-NMR measurements of the spin-spin relaxation times (T_2) were performed with the Hahn spin-echo method on a Varian Unity Inova spectrometer operating at 600 MHz. The samples with various cross-linking densities were dissolved in CDCl₃ (1 mg mL⁻¹). The typical acquisition parameters were 5.6 μ s $\pi/2$ r.f. pulses, 6 kHz spectral bandwidth, and 3 s relaxation delay at room temperature. Analysis and processing of free induction decays (FIDs), spectra, and spin-echoes were carried out with Mestrelab Research's Mnova NMR software.

2.6 Characterizations

Size exclusion chromatograph (SEC) measurements were performed on a Waters system equipped with a refractive index detector (RI 410) and a photodiode array detector (PDA 996). THF was used as the eluent at an elution rate of 1 mL min⁻¹, while PS standards were used for calibration. Generally, ¹H NMR spectra (in CDCl₃, unless otherwise stated) were obtained with a Bruker AC 300 MHz spectrometer. The UV light at $\lambda > 310\text{ nm}$ used for the photo-cross-linking reaction was generated from a UV-vis spot curing system (Novacure) with a 320–500 nm

filter and the intensity was $\sim 900 \text{ mW cm}^{-2}$. For the photocleavage of cyclobutane rings (photo-de-cross-linking), a UV-C Air sterilizer lamp (1.25 W) peaked at $\lambda = 254 \text{ nm}$ was used at a distance of 5 cm to the nanoparticle solution. During the photo-cross-linking and de-cross-linking, the dimerization degree of coumarin was followed by recording UV-vis spectra on a Varian 50 Bio UV-vis spectrophotometer. The sizes of nanoparticles were examined using a Hitachi H-7500 transmission electron microscope (TEM) operating at 60 kV. Samples were prepared by casting 3–5 μL solution on a carbon-coated copper grid, followed by drying at room temperature. Glass transition temperatures (T_g) of polymer samples were measured by using a TA Q200 differential scanning calorimeter (DSC) with a heating and cooling rate of $10 \text{ }^\circ\text{C min}^{-1}$. The viscosity measurements were carried out at $22 \text{ }^\circ\text{C}$ on a Viscotech rheometer (Rheologica Instruments AB) using a cone-plate geometry (30 mm diameter, 2° cone).

3. Results and discussion

3.1 Preparation and characterization of SCNPs

As presented in Fig. 1b, the investigated coumarin-containing polymer is a random copolymer of poly(*N,N*-dimethylaminoethyl methacrylate) bearing a number of CMA comonomer units, referred to as P(DMAEMA-*co*-CMA) hereafter. RAFT copolymerization was conducted at $65 \text{ }^\circ\text{C}$ to yield two samples with different coumarin mole ratios (P1 and P2). In order to prepare well-defined polymer SCNPs, polymers were required to have a high molecular weight and narrow polydispersity. With the accurate control over the molecular weight by RAFT polymerization (the mole ratio of DMAEMA and CPDB was kept $\sim 1000 : 1$), the two samples have molecular weight $\sim 100\,000 \text{ g mol}^{-1}$ and polydispersity ~ 1.2 , which we found are good enough for preparing SCNPs through intrachain photo-cross-linking.

To promote efficient single chain collapse *via* intrachain photo-cross-linking, the photodimerization of coumarin should be conducted with the polymer dissolved in a good solvent at a very low concentration in order to avoid the interchain cross-linking.^{13–20} As mentioned above, coumarin side groups in the polymer can undergo a photodimerization reaction upon absorption of photons at $\lambda > 310 \text{ nm}$. If the dimerization occurs between two coumarin groups on the same polymer chain adopting a coil conformation, it gives an intrachain cross-linking point. Chain collapse can be expected to take place when the chain is subjected to the constraint of a certain number of intrachain cross-links and undergoes the coil-to-globule conformational transition.

Either P1 or P2 was dissolved in THF at 1 mg mL^{-1} ; then the solution was exposed to $\lambda > 310 \text{ nm}$ UV light (900 mW cm^{-2}) for photo-cross-linking. The occurrence of photodimerization of coumarin groups in the dilute solution was first monitored by UV-vis spectroscopy. UV-vis spectra of P2 recorded over irradiation time are shown in Fig. 2. The absorption peak of coumarin at $\sim 320 \text{ nm}$ displays a continuous decrease with increasing irradiation time, indicating a growing degree of dimerization. From the spectra, the dimerization degree could reach $\sim 75\%$ after 1 h irradiation. Compared with the photodimerization in BCP micellar aggregates in water,^{22,24,25} the

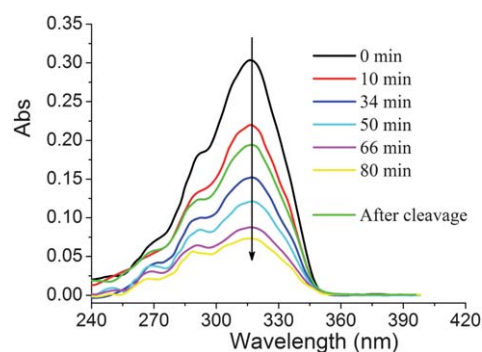


Fig. 2 UV-vis spectra of P1 in THF (1 mg mL^{-1} , 12 mL) recorded after UV irradiation ($\sim 900 \text{ mW cm}^{-2}$), showing photodimerization (cross-linking) upon $>310 \text{ nm}$ irradiation and partial photo-cleavage (de-cross-linking) upon $<260 \text{ nm}$.

photoreaction appears to proceed more slowly. This is likely caused by the good solvation of coumarin groups in THF, which makes them more difficult to have two coumarin groups at a close distance required for dimerization. Upon changing the UV light wavelength to $\lambda < 260 \text{ nm}$, the reverse photo-cleavage reaction occurs partly, with the dimerization degree reduced from 75 to 38% after 2 h irradiation.

SEC measurements show that under the experimental conditions the photodimerization takes place intramolecularly and the resulting cross-linking indeed could lead to chain collapse resulting in the formation of SCNPs. It is known that the apparent molecular weight will increase if the cross-linking occurs intermolecularly, while it will decrease if the cross-linking is intramolecular.^{15–19} SEC traces of P1 and P2 recorded at various UV irradiation times (up to 1 h) are given in Fig. 3, and the corresponding changes in the apparent molecular weight (M_n) and the molecular weight distribution plotted as a function of coumarin dimerization degree are also shown.

For both polymers, the elution peak shows a continuous increase of retention time, indicating the occurrence of intramolecular cross-linking. The apparent molecular weight decreases from $\sim 110\,000$ to $\sim 74\,000 \text{ g mol}^{-1}$ for P1 and from $\sim 104\,000$ to $75\,000 \text{ g mol}^{-1}$ for P2. By contrast, the polydispersity of cross-linked polymers increases slightly which is possibly caused by the different cross-linking degrees of each individual polymer chain. According to the results, P1 behaves in the same way as P2 despite a lower content of coumarin groups. And also quite surprisingly, after exposing the formed SCNPs to UV light at $\lambda < 260 \text{ nm}$ for the photocleavage reaction of coumarin, SEC measurements found no shift of the elution peak towards shorter retention times. In other words, the photo-de-cross-linking could not induce the reverse globule-to-coil transition. As mentioned above, under the used conditions, the photocleavage reaction occurs only partially due to a photostationary state.²² It appears that the remaining intrachain cross-linking (with $\sim 38\%$ dimerization of coumarin) was enough to preserve the globule conformation and retain polymer chains in the collapsed state.

SCNPs prepared through intrachain photo-cross-linking were further characterized by means of solution viscosity, DSC and TEM. The results of viscosity and DSC are shown in Fig. 4 and 5, in comparison with the linear polymer precursor. The relative

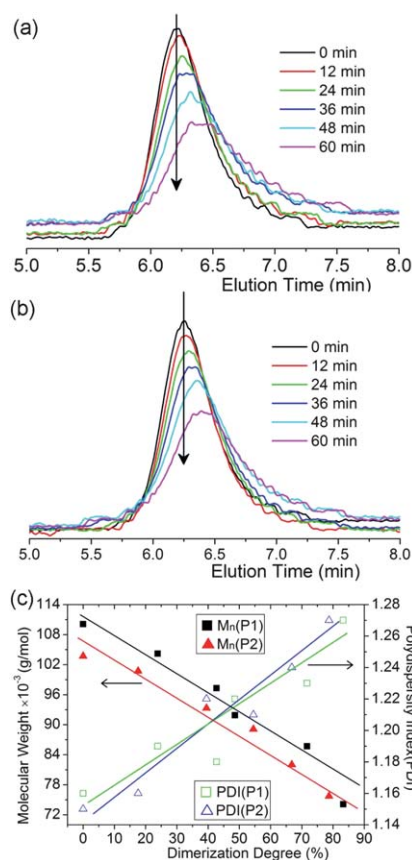


Fig. 3 SEC traces of P1 (a) and P2 (b) with different irradiation times and the change of the apparent molecular weight and polydispersity of P1 and P2 as a function of coumarin dimerization degree (c).

viscosities of the linear polymer P2 and its SCNPs in THF solution were measured at room temperature (Fig. 4). The fast increase of the relative viscosity of the linear polymer with increasing polymer concentration is typical of coiled polymer chains having strong intermolecular interactions with the solvent. By contrast, the relative viscosity of SCNPs increases only slightly when increasing the concentration up to 20 mg mL⁻¹. This behavior is indicative of collapsed SCNPs that have less interaction with the solvent and induce less important increase of the solution viscosity. Likewise, the glass transition temperature (T_g) increases from 40 °C for linear P2 to 79 °C for its SCNPs with a dimerization degree of 72%, which confirms the

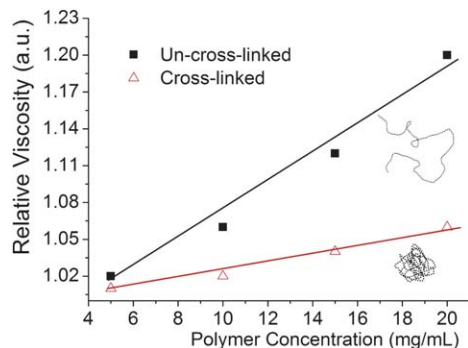


Fig. 4 Relative viscosity of P2 linear polymer and its SCNPs in THF solution at various concentrations.

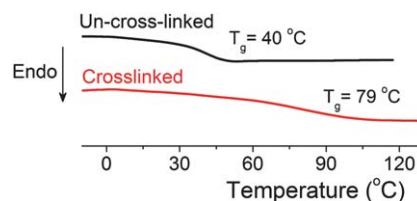


Fig. 5 DSC curves (second heating scan) for P2 linear polymer and its SCNPs.

loss of chain mobility after photo-cross-linking. The broader glass transition region of the SCNPs also suggests that the cross-linking degree of individual chains may vary, which is consistent with the slight increase of polydispersity after photo-cross-linking (Fig. 3).

The formed SCNPs could be visualized by TEM. Fig. 6 shows an image of nanoparticles of P2 cast from a THF solution and an image of nanoparticles cast from an aqueous solution, with, in both cases, an inset showing a section of the image with a higher magnification. Cast from THF, the nanoparticles have diameters in the range of 30–60 nm, which are much larger than the typical sizes of SCNPs reported (10–20 nm).^{14–19} However, after solvent exchange through dialysis, nanoparticles in water appear to have smaller sizes corresponding to SCNPs (10–20 nm). The larger size in THF could be explained by the fact that THF is a good solvent for the polymer. When cast in a solvated state, the SCNPs have a loose structure and can flatten easily on the surface of the copper grid during the solvent evaporation. Aggregation of SCNPs during the drying process also cannot be ruled out. In water, which is a non-solvent for the coumarin-containing P(DMAEMA-co-CMA) (P2 has 13% of coumarin), contraction of SCNPs should occur, making them more dense, compact and thus smaller. Additionally, after dialyzing against water, SCNPs

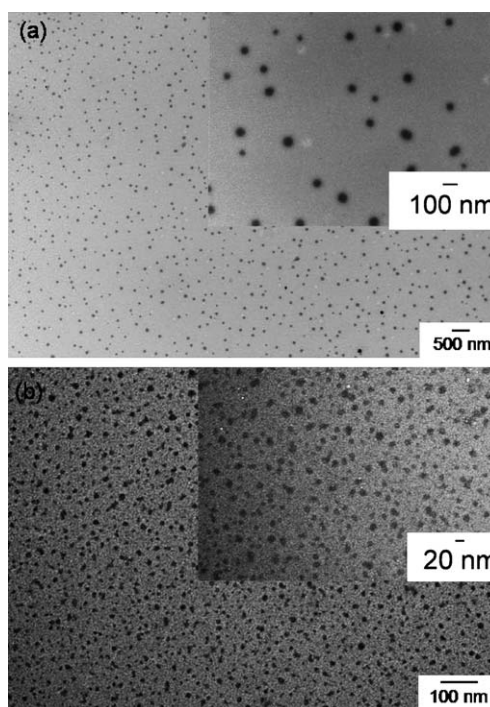


Fig. 6 TEM images for SCNPs of P2 in THF (a) and H₂O (b).

of P2 are rather stable in aqueous solution; no irreversible precipitation was observed after three months.

3.2 ^1H NMR spectroscopic investigation of SCNPs

To get more insights into the conformational transition of polymer chains from random coil to globule in the process of intrachain photo-cross-linking induced SCNP formation, we carried out an investigation by means of ^1H NMR spectroscopy. Fig. 7 shows the NMR spectra of P2 in CDCl_3 (1 mg mL^{-1}) before and after UV irradiation for photo-cross-linking. The assignments of resonances to various protons of the side chain of DMAEMA and CMA are indicated in the spectra. With dimerization degree at 71%, the intensities of CMA peaks (especially those of aromatic protons) decrease due to the cross-linking reaction. The NMR integrals of aromatic protons *c* of coumarin at $\sim 6.16 \text{ ppm}$ and *d* and *e* of methylene groups of side chains at $\sim 4.3 \text{ ppm}$ decreased by about 55% and 35%, respectively. New resonance peaks appear at 3.0–3.8 ppm which are assigned to the formed cyclobutane rings. Diminished signals of DMAEMA units after cross-linking are also noticeable ($\sim 5\%$), which should be accounted for by the transition to the globular conformation which restricts the mobility of polymer chains. Since ^1H spin–spin relaxation time (T_2) is sensitive to molecular motion,^{29–31} we conducted NMR relaxation time measurements.

Fig. 8a shows the decay curves of the protons of $-\text{CH}_2\text{O}-$ group on the side chain of PDMAEMA obtained with the Hahn spin-echo method at various photodimerization degrees of coumarin groups in P2 (1 mg mL^{-1}). All decay curves are approximately bi-exponential (*i.e.*, two T_2), which indicates the existence of two types of molecular motions in solution. The short T_2 arises from a fast decaying component that represents the population of chain segments undergoing a slow motion, *i.e.*, with restricted mobility. Conversely, the long T_2 is related to a slow component of chain segments that have a fast motion due to higher mobility. Since the NMR measurements were conducted using the same dilute polymer solution as for the preparation of SCNPs, interchain interaction is assumed to be

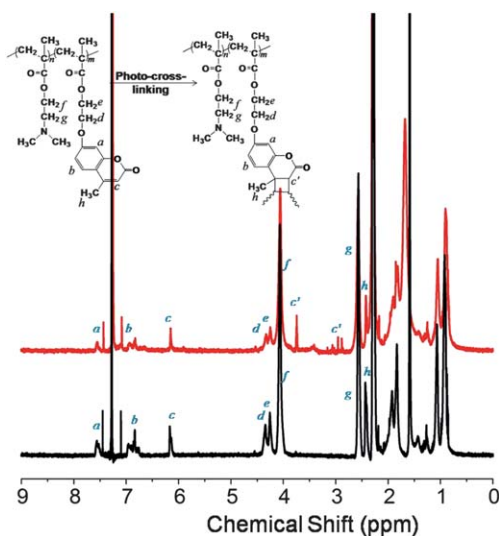


Fig. 7 NMR spectra of P2 in CDCl_3 before (bottom) and after (top) cross-linking.

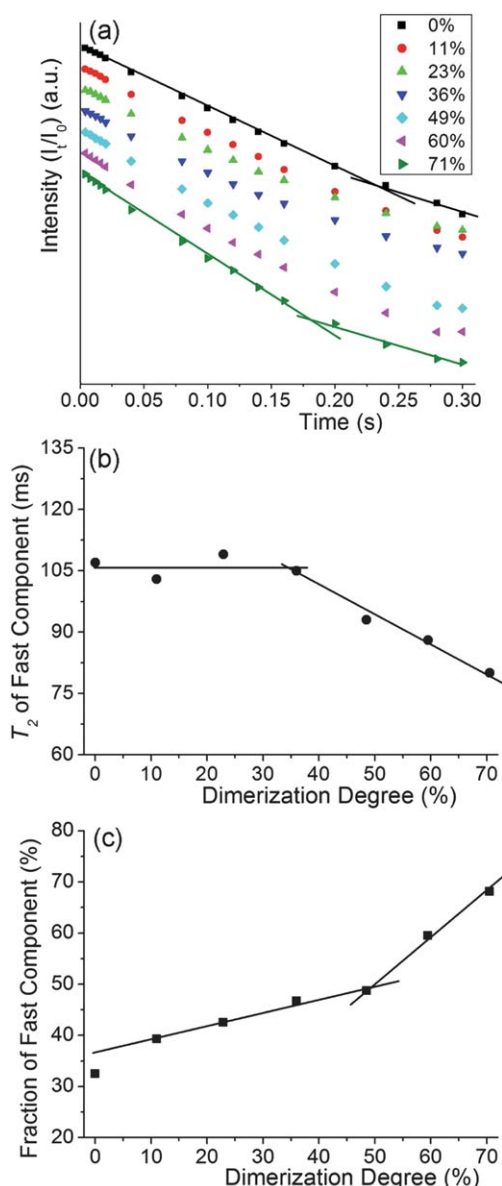


Fig. 8 (a) T_2 decay curves of $-\text{CH}_2\text{O}-$ groups on the side chain of PDMAEMA (peak *f* in Fig. 7) in CDCl_3 with various photodimerization degrees from C0 to C6: 0%, 11%, 23%, 36%, 49%, 60% and 71%, respectively; (b) T_2 of fast component of $-\text{CH}_2\text{O}-$ groups vs. dimerization degree; (c) fraction of fast component of $-\text{CH}_2\text{O}-$ groups vs. dimerization degree.

negligible. The molecular interactions leading to the two populations of chain segments with different mobilities should arise mainly from the interaction between segments within the same polymer chain (intrachain polymer interaction) and between chain segments and solvent molecules (polymer–solvent interactions), which correspond to the fast and slow decay component, respectively. For example, for P2 before cross-linking, $T_{2,\text{fast}}$ is 107 ms with a fraction 31% for the fast component (more rigid segments subjected mainly to intrachain polymer interaction), while $T_{2,\text{slow}}$ is 140 ms with a fraction of 69% for the slow component (more solvated, flexible segments mainly exposed to interaction with CDCl_3).

With increasing the cross-linking density, the T_2 values of the fast component and its fraction are plotted as a function of dimerization degree in Fig. 8b and c. For dimerization degrees lower than $\sim 36\%$, T_2 is 105–110 ms. Upon further increase of the dimerization degrees from 36% to 71%, the T_2 values rapidly decrease from 105 to 80 ms, indicating a loss of mobility of chain segments for the fast component. For the slow component, T_2 varies in the range of 140 to 160 ms, indicating that chain segments subjected to polymer–solvent interactions are influenced relatively weakly by the chain cross-linking. As for the fraction of fast component, it shows an abrupt increase at high dimerization degrees. These NMR results indicate the conformational transition of polymer chain from random coil to globule occurring at a dimerization degree $>36\%$. When the dimerization degree reaches 71%, the resulting SCNPs have a fast $T_2 \approx 80$ ms and $\sim 68\%$ of chain segments in the fraction of fast component with a reduced mobility. It is understandable that in the SCNPs less chain segments are exposed to solvent molecules and the fraction of solvated chain segments is smaller.

3.3 *In situ* synthesis of gold nanoparticles using SCNPs as a nanoreactor

Because of the coordination ability of the tertiary amine in PDMAEMA with many metals, this polymer can be used to synthesize colloidal metal nanoparticles, such as gold nanoparticles (AuNPs), without any additional reductants.²⁸ We investigated the use of SCNPs of P(DMAEMA-*co*-CMA) as a nanoreactor for the synthesis of AuNPs. This was first conducted in THF solution at Au/N = 1/10 (mole ratio of HAuCl₄ to the amine groups of PDMAEMA). Since the cross-linking density can easily be tuned with the photodimerization degree of coumarin, we wanted to know how this parameter could affect the formation of AuNPs. For this experiment, three THF solutions of P2 (0.5 mg mL⁻¹) with different dimerization degrees (0%, 27% and 64%) were mixed with the same amount of HAuCl₄ and stirred at room temperature. Upon reduction of HAuCl₄ leading to the formation of AuNPs, the appearance of solution changed from colorless to dark red, which is accompanied by a gradual increase of absorption at ~ 530 nm corresponding to the surface plasmon resonance (SPR) of AuNPs. We found that the cross-linking density, thus the aggregation or conformation of single polymer chain, could exert a profound effect on the rate of AuNP formation. This can be noticed from the photographs shown in Fig. 9a. With the same reaction time, the solution with more cross-linked P(DMAEMA-*co*-CMA) shows a darker red color, indicating the formation of more AuNPs. Fig. 9b shows the UV-vis spectral change over time for the polymer solution with 64% dimerization degree. The increase in the amount of AuNPs can be seen from the increased absorbance at 530 nm. Fig. 9c shows the plots of absorbance at 530 nm *vs.* time for the three polymer solutions. The effect of chain cross-linking becomes evident. The apparent rate of AuNP formation in the SCNP solution (64% dimerization degree) is roughly twice and four times faster than in the polymer solution with a dimerization degree of 27% and in the un-cross-linked polymer solution, respectively.

The observed dependence of AuNP formation rate on the single polymer chain cross-linking degree is interesting. It means

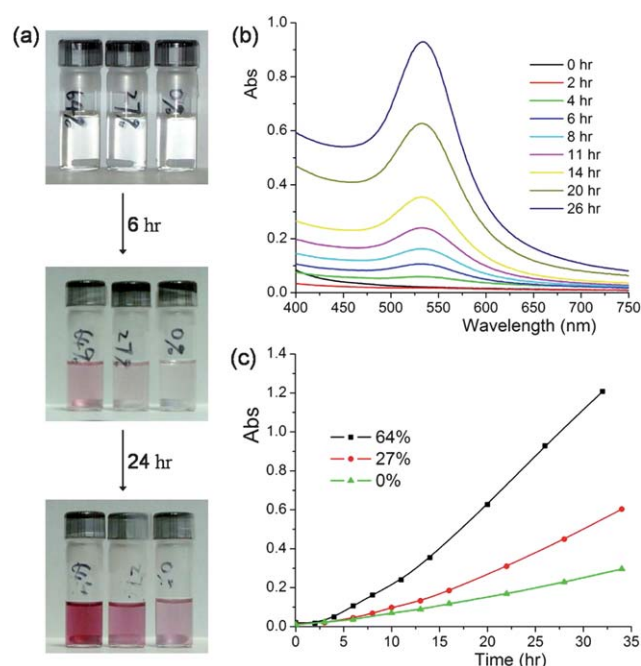


Fig. 9 (a) Photos showing the effect of photodimerization degree of coumarin on the rate of AuNP formation in THF solution of P(DMAEMA-*co*-CMA) (from left to right: 64%, 27% and 0%); (b) UV-vis spectra of the reduction solution with SCNPs at a dimerization degree of 64% at various reaction times; and (c) increase in the absorbance of AuNPs at 530 nm over reaction time for solutions of P(DMAEMA-*co*-CMA) with different dimerization degrees.

that the kinetics can be easily tuned by adjusting the intrachain cross-linking. The controllable photo-cross-linking degree of coumarin-containing polymers offers an obvious advantage. This phenomenon is understandable from the mechanism of AuNP formation. The tertiary amine groups of PDMAEMA act as both reductant and stabilizer of AuNPs in the reaction *via* the absorption of AuCl₄ ions and coordination bonding between gold and amine groups. When polymer chains are collapsed and packed into SCNPs, more AuCl₄ ions would be concentrated around the polymer chains and AuNPs could be more easily retained.

Following the same line of thought, the more compact structure of SCNPs in water should speed up the formation of AuNPs. Indeed, using the same experimental conditions except the solvent change from THF to water, the absorption of SPR of AuNPs appeared only after a few minutes. Fig. 10a shows the UV-vis spectrum after 180 min reaction, the inset is a TEM image of the formed AuNPs (6–9 nm in diameter). By following the UV-vis spectral change, the apparent rate of AuNP formation in aqueous solution is shown in Fig. 10b. The whole reduction process in water is finished in ~ 180 min at room temperature, which is much faster than the reaction in THF solution. And this reaction rate is in good accordance with the reported results using a BCP of PDMAEMA.²⁸

4. Conclusions

We demonstrated a novel and facile method for preparing polymer SCNPs. It is based on incorporating a number of coumarin

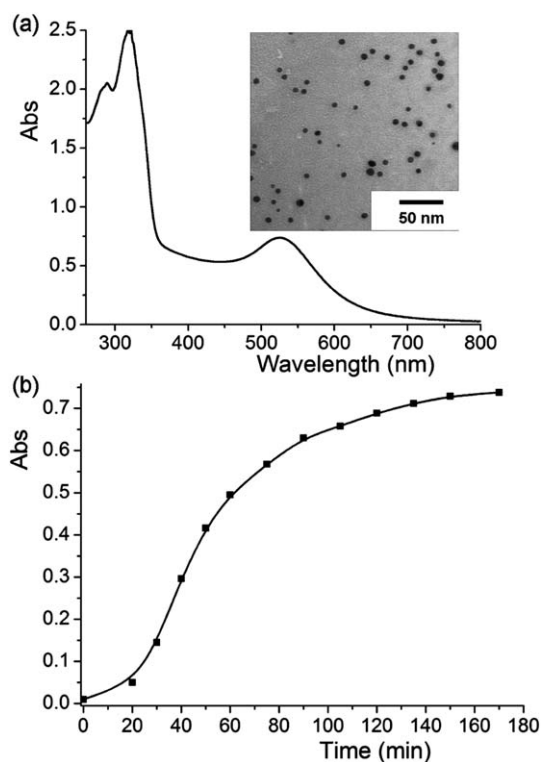


Fig. 10 (a) UV-vis spectrum of AuNPs formed in aqueous solution of SCNPs of P2 recorded after 180 min reaction; and (b) change in absorbance at 530 nm vs. reaction time.

side groups into a polymer and using the easily controllable photodimerization of the chromophore to cross-link single polymer chains intramolecularly in a dilute solution. Using random copolymers of P(DMAEMA-*co*-CMA) containing 7 or 13 mol% of coumarin, we found evidence of SCNPF formation upon intrachain photo-cross-linking. ^1H NMR spin-spin relaxation time (T_2) measurements revealed that the coil-to-globule transition (chain collapse) occurred when the cross-linking degree reached a certain threshold (>36% dimerization degree with the sample containing 13% of coumarin), which is accompanied by a sharp increase of the fraction of chain segments having reduced chain mobility (fast relaxation time) and the concomitant drop of the fraction of chain segments having a greater chain mobility (solvated fraction with the slower relaxation time). Furthermore, we showed that such SCNPs could be used as a nanoreactor for the synthesis of AuNPs, and found that for P(DMAEMA-*co*-CMA) in a good solvent like THF, the rate of AuNP formation is sensitive to the intrachain cross-linking density determined by the dimerization degree of coumarin groups (faster with increasing the cross-linking density). This provides a means to optically tune the kinetics of AuNP formation.

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