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Synthesis of thermo- and photo- responsive polysiloxanes with tunable phase separation via aza-Michael addition

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Two kinds of thermo- and photo- dual-responsive polysiloxanes (DRPSs) with functional pendent groups, N-isopropyl amides and azobenzene (Azo) or salicylideneaniline (SA) were synthesized through a facile, effective, and catalyst-free aza-Michael addition of poly(aminopropylmethyl-siloxane) with N-isopropyl acrylamide and N-azobenzene acrylamide or Nsalicylaldehyde acrylamide. The chemical structrures of DRPSs were systematically characterized by FT-IR, H NMR and UV-Vis spectrum. The as-prepared DRPSs with lower Azo or SA contents exhibited lower critical solution temperature (LCST)type phase transition in water, which is reversible and can be controlled by temperature and UV light. The effect of Azo and SA content on responsive properties of DRPSs are examinated in detail. The LCST decreased with the increasing Azo or SA content. Once the content of Azo or SA reached up to 5.7% or 8.2% respectively, DRPSs can not dissolved in water even in ice bath. Higher values for the LCST were measured after irradiation of the polymer solutions due to the higher polarity of cis-Azo and keto-SA conformation, induced by irradiation. The differences of cloudy points between the irradiated and the non-irradiated DRPSs aqueous solutions increased up to 3.4 °C and 9.8 °C when combined with 3.8% Azo and 5.8% SA units, respectively.

1 Introduction

Polysiloxane is an appealing material for clinical and medical treatments, because of its outstanding physiological inertness, non-toxicity, and biocompatibility.^{1,2} To satisfy smart clinical and biomedical applications, such as controllable drug delivery, smart bioactive surfaces, and selective bioseparation, a few smart polysiloxanes with controllable hydrophobic/hydrophilic property have been synthesized through modification of polysiloxane matrix using guest smart polymers or inlaving polysiloxane into amphipathic block copolymers.³⁻⁶ However, the polysiloxane segments in these polymers merely serve as accessories and show no stimuliresponsive capacities due to their intrinsic hydrophobicity, and these poysiloxanes are non-water-soluble, limited their usage in smart applications. Therefore, it is highly desirable, yet synthetically a challenge to the development of methodologies to synthesize stimuli-responsive polymers with polysiloxane as backbones. Recently, we designed and synthesized a series of high thermo-responsive polysiloxanes with high sensitivity and controllable phase separation behaviour, due to its flexible Si-O-Si backbone, based on a facile, effective, and catalyst-free aza-Michael addition.7,8

Besides responsive to a single stimulus, recent a few

researches interest in polymers that show responsive behaviours to multiple stimuli.⁹⁻¹² In addition, polymers that are responsive to light and temperature are very appealing and important for applications, because light is everlasting, clean, non-invasive, a wide range of wavelengths, and features high spatiotemporal resolution. Accordingly, there have been several reports on thermo-responsive polymers that contain photo-responsive moieties.¹³⁻¹⁸ Azobenzene (Azo) groups¹⁹⁻²² and salicylideneaniline (SA) moieties^{23,24} have been applied as photochromic groups to establish photo-responsive polymers, photo-controlled benefitting from their reversible isomerization. The former show a reversible isomerization from trans- to cis-configuration upon irradiation²⁵⁻²⁸ and the latter exhibit isomerization from the enol- into the keto-form upon irradiation with UV light.²⁹⁻³¹ Polysiloxanes with photoresponsive property have also been gaining attentions, 32-37 however water-soluble ones with thermo- and photo-tunable phase-separation have not been reported.

In this article, we present a facile method for synthesis thermo- and photo- dual-responsive polysiloxanes (DRPSs) featuring N-isopropyl amide (NIPAs) and Azo or SA groups, in which, NIPAs served as thermo-responsive groups, while Azo and SA served as the corresponding photo-responsive moieties. The synthesis was successfully achieved via catalyst-free aza-Michael addition of amino-containing polysiloxane (PAPMS) with N-isopropyl acrylamide (NIPAAm), and N-azobenzene acrylamide (AAM-Azo) or N-salicylaldehyde acrylamide (AAM-SA). In specific, aza-Michael addition yields no by-products and exhibits high function group tolerance and high conversions at room temperature.^{38,39} The polysiloxanes

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ARTICLE

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exhibit a lower critical solution temperature (LCST) in aqueous solution, which was dependent on the amount of incorporated NIPAs, and Azo or SA groups, and the isomerization state of the respective Azo or SA groups. The addition process and thermo- and light- controlled phase separation behavior of asprepared polysiloxanes are discussed in details.

2 Experiments

2.1 Materials

All chemicals and solvents were commercially available and used as received unless otherwise stated. *p*-Nitroaniline, acryloyl chloride, salicylaldehyde, 4-aminoazobenzene and N-isopropylacrylamide of analytically pure were obtained from Energy Chemical. 3-aminopropyl methyldiethoxysilane of industrial grade was purchased from Shenzhen Changhao Technology Company and used after distillation under reduced pressure and were determined by ¹H NMR. 2,4,6,8-tetraaminopropyl-2,4,6,8-tetraamethyl cyclotetrasiloxane (D₄-AP) was synthesized as described in the literature.⁷

2.2 Instrumentation

FT-IR spectra were recorded using a Bruker TENSOR 27 FT-IR spectrometer instrument within the range of 4000-400 cm⁻¹ working at 4 cm⁻¹ resolution. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer in DMSO-d₆. The molecular weights and molecular weight distributions (Mw/Mn) of samples were determined by gel permeation chromatography (GPC) measurements performed on a Milford MA Waters 515 liquid chromatography equipped with a Waters 2414 refractive-index detector. Samples were run in THF at 40 °C at a rate of 1 mL·min⁻¹ with respect to polystyrene standards. UV/vis spectra were recorded on а TU-9001 photospectrometer. LCSTs of the polysiloxnaes were determined by turbidimetry in water at a concentration of 10 mg·mL⁻¹. The optical transmittance of a light beam (λ =700 nm) through the 1.0 cm sample quartz cell of the photospectrometer was monitored as a function of temperature. The heating rate was 0.5 °C·min⁻¹. The LCST were defined as the temperature at which a transmission of 50 % was observed. The irradiation experiments were conduct with an oriel instruments 500 W mercury lamp with a 365 nm filter in a 1 cm diameter quartz cell.

2.3 Synthesis of N-salicylaldehyde acrylamide (AAM-SA)

p-Nitroaniline (1.38 g, 10 mmol) and triethylamine (1.20 g, 12 mmol) were dissolved in THF (100 ml) and cooled to 0 °C and stirring. Then, acryloyl chloride (1.18 g, 12 mmol) was added into the solution and stirred for overnight. THF was evaporated under reduced pressure, and the residue was dissolved in acetic ether (100 mL) and washed with a saturated aqueous solution of NaHCO₃ (50 mL) for three times. The organic layer was dried with magnesium sulfate, filtered, and distilled under reduced pressure and yellow crude powder product (1.76 g) was obtained. Then, the powder was dissolved in a 5:1 mixture of ethanol and water (100 mL). Iron powder (1.10 g), and saturated ammonium chloride solution

(10 mL) was added into the solution and refluxed for overnight. The solution was filtered and distilled under reduced pressure and crude powder product was obtained. Then, the powder was dissolved in ethanol (50 mL) and treated with salicylaldehyde (1.22 g, 10 mmol). Under vigorous stirring, the mixture was refluxed for 3 h. The ethanol was removed under reduced pressure and the residue was purified by silica gel chromatography using acetic ether/Hexanes (1:1) as eluent to yield AAM-SA (76 %). ¹H NMR (400 MHz, DMSO-d6): δ 13.22 (1H, s), 10.31 (1H, s), 8.98 (1H, s), 7.78 (2H, d), 7.64 (1H, m), 7.42 (3H, m), 6.98 (2H, m), 6.45 (1H, m), 6.29 (1H, m), 5.79 (1H, m). ¹³C NMR (100 MHz, DMSO-d₆): δ 163.61, 162.51, 160.73, 143.60, 138.61, 133.46, 132.89, 132.26, 127.48, 122.37, 120.57, 119.56, 117.02 ppm.

2.4 Synthesis of N-azobenzene acrylamide (AAM-Azo)

4-aminoazobenzene (1.97 g, 10 mmol) and triethylamine (1.21 g, 12 mmol) were dissolved in CH_2Cl_2 (90 mL), and acryloyl chloride (1.09 g, 12 mmol) was dissolved in another CH_2Cl_2 (10 mL). The latter was dropwise added into the former for 0.5 h under ice-water bath and vigorous stirring for overnight. The obtained mixture was filtered and the filtrate was concentrated under reduced pressure and purified by silica gel chromatography using acetic ether/Hexanes (2:3) as eluent to yield AAM-Azo (86 %). ¹H NMR (400 MHz, DMSO-d₆): δ 10.54 (s, 1H), 7.92–7.85 (m, 6H), 7.62-7.54 (m, 3H), 6.55-6.29 (m, 1H), 6.35-6.29 (m, 1H), 5.85-5.78 (m, 1H). ¹³C NMR (100 MHz, DMSO-d₆): δ 163.75, 152.76, 149.29, 140.38, 131.00, 130.96, 129.21, 128.74, 124.17, 122.89, 120.14 ppm.

2.5 Synthesis of poly(aminopropylmethylsiloxane) (PAPMS) and thermo- and photo-responsive polysiloxane (DRPSs)

D₄-AP (23.4 g, 0.05 mol) was injected with nitrogen into a three-neck flask equipped with a mechanical stirrer. Then, KOH (0.05 g, 0.2 wt.-%) and DMSO (0.23 g, 1.0 wt.-%) was added to the mixture, and the temperature was increased to 50 °C. The viscosity of the reaction mixture sharply increased after 1 h or so. AP₂-PSi₂ (0.50 g, 2 mmol) was added rapidly to the flask, and the reaction was equilibrated for 5 h. PAPMS was obtained after the mixture cooled to room temperature and neutralized by an equimolar acetic acid with KOH. Then, PAPMS (1.0 g), NIPAAM (0.29 g, 30 mol.-%) and AAM-SA (0.095 g, 4 mol. %) or AAM-Azo (0.09 g, 4 mol. %) were dissolved in DMF (10 mL), and stirred for 24 h at 30 °C. Smart polysiloxanes were obtained after the DMF was removed by reduced pressure and vacuum drying. A viscous product was obtained. The contents of NIPAs and Azo/SA in the obtained polysiloxane were controlled by the feed molar ratios of NIPAAM and AAM-SA/AAM-Azo in systems.

3 Results and discussion

Scheme 1 shows the synthetic scheme of DRPSs via catalystfree aza-Michael addition of PAPMS (molar weight of 11520 $g \cdot mol^{-1}$, about 97 Si-O units) with NIPAAm and AAM-Azo or AAM-SA using DMF/ethanol (8:2) as solvent at room temperature. The PAPMS was synthesized through the ring-

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opening polymerization of 2,4,6,8-Tetraaminopropyl-2,4,6,8tetramethyl cyclotetrasiloxane (D₄-AP) using KOH as a catalyst, DMSO as an accelerator and 1,3-bis(3-aminopropyl)tetramethyldislloxane (AP₂-PSi₂) as an end-capping reagent.^{7,8} AAM-Azo was synthesized by amidation of aminoazobenzene with acryloyl chloride.^{40,41} AAM-SA was obtained by amidation of *p*-nitroaniline with acryloyl chloride and followed by a reduction reaction with iron powder and a Schiff base reaction with salicylaldehyde.^{42,43} These guest molecules, NIPAAm, AAM-SA, and AAM-Azo, which are all α , β -unsaturated carbonyl compounds possessing electron drawing group (C=O), served as receptors of the aza-Michael addition. Meanwhile, amino groups in PAPMS can serve as nucleophiles and bases. Thus, the addition can be high-efficiently conducted at room temperature without any catalyst, and shows good tolerant to other active groups.⁴⁴⁻⁴⁶ Analogous aza-Michael reactions of amino groups with acrylamide or acrylate derivatives have been reported as novel polymer synthesis strategies, especially for poly(amido amine)s⁴⁷⁻⁴⁹ and poly(ester amine)s⁵⁰⁻⁵⁴ respectively. In specific, the reaction yields no by-products and exhibits high function group tolerance and high conversions at room temperature, which provides a convenient and practical method for the establishment of smart polysiloxane systems. Primary amines add to electron poor alkenes that are susceptible to nucleophilic attack to give secondary and tertiary derivatives. The first product formed, the monoadduct, can react further to give the tertiary derivative, or bisadduct.^{55,56} Herein, DMF/ethanol (8:2) mixed solvent was selected for the addition, because DMF was more conducive to form a mono-addition product, 57,58 in addition, the obtained AAM-Azo and AAM-SA can be dissolved in DMF. Ethanol, a general proton solvent, can promoted rapid proton transfer







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ARTICLE

and to stabilize charged intermediates and was considered as good solvent to accelerate the Michael addition. Furthermore, amino groups in PAPMS are much more than α , β -unsaturated carbonyl compounds in molar, thus the bis-addition are indiscernible in NMR.

As shown in Fig. 1, the obtained DRPSs can be dissolved in water at lower temperature, and precipitated from solvent when the temperature increased up to a certain value, namely cloudy point. This phenomenon, analogous to reported poly(NIPAAm)s,⁵⁹⁻⁶¹ can be attribute to thermo-dependent hydrogen bonding effect of the N-isopropyl groups in polymers with water molecules, which become weak with increased temperature. Simply, at low temperatures, the polysiloxane chains are in the energetically favoured hydrated state, as water molecules associated with amino groups form hydrogenbonded cage-like structures around the hydrophobic isopropyl groups. As the temperature increases, the hydrogen bonding becomes weaker. Above the cloudy point, intramolecular hydrogen bonds between C=O and N-H groups in the chains result in a compact and hydrophobic collapsed conformation of polymer chains and polysiloxane precipitation from water. The phase separation behaviour, that is to say the cloudy point of the obtained polysiloxane is affected significantly to the amount of attached Azo or SA and UV irritation, because of the combination of Azo or SA groups in the polysiloxane as pendant groups, which will be discussed in details in the later.

The polymer structures were analysed by ¹H NMR, and FT-IR. As shown in Fig. 2, the signals of α , β -unsaturated double



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Runs	NIPAs (mol%) ^[a]	Azo or SA	(mol%) ^[b]	LCST Un-irradiated (°C)	LCST irradiated (°C)	∆LCST(°C)
P0a	30.3	Azo	0	43.2	43.2	0
P1a			1.8	35.1	36.9	1.8
P1b			3.8	22.3	25.7	3.4
P1c			5.7	none	none	/
P2a	29.8	SA	1.9	37.9	40.0	2.1
P2b			3.9	27.9	33.5	5.6
P2c			5.8	12.4	22.2	9.8
P2d			8.2	none	none	/
P0b			0	28.9	28.9	0
P2f	39.8	SA	2.1	18.6	19.7	1.1
P2g			4.1	none	none	/

[a] Contents of NIPAs obtained by ¹H NMR. [b] Contents of Azo or SA obtained by ¹H NMR.

bonds of acrylamide derivatives (NIPAAm, AAM-Azo and AAM-SA) about at 4.2, 6.1, and 6.2 ppm⁶² totally vanished from obtained DRPSs (taking POa, P1b and P2b for examples), indicating a complete conversion of aza-Michael addition. Meanwhile, peaks displayed at 2.2 and 2.8 ppm in obtained polymers further justified that -NH-CH2-CH2-CO- groups newly formed after the addition. Additionally, the characteristic signal of $-CH(CH_3)_2$ at 1.0 ppm and aromatic proton signals at the range of 7.0 to 8.0 ppm also indicated successful addition. The peaks at 0.0, 0.5, and 1.2 ppm were -Si-CH₃, -Si-CH₂-, and -Si-CH₂-CH₂assigned to respectively.⁶³ The conversions of NIPAAm, AAM-Azo, and AAM-SA into DRPSs were determined from the characteristic signals of $-CH(CH_3)_2$ and aromatic ring relative to the signal of -Si-CH₂- at 0.5 ppm. The results are listed in Table 1.

The FT-IR spectrum of polymer PAPMS, P0, P1b and P2b were shown in Fig. 3. The characteristic singles at 3,200–3,400 cm⁻¹ belonged to the stretching vibration of NH₂. The peaks at 1,258 cm⁻¹, 1,090 cm⁻¹, and 800 cm⁻¹ assigned to the vibration features of Si-C, the asymmetric bending of Si–O–Si, and symmetric stretching of Si-O respectively.^{64,65} Besides, clearly visible singles at 3,058 cm⁻¹ (overtone bands of stretching vibration of NH), 1,660 cm⁻¹ (stretching vibration of the C=O) and 1,550 cm⁻¹ (bending vibration of the NH) were also

Fig. 3 ET-IR spectra of DRPSs PAPMS, POa, P1b, and P2b

observed in as-prepared polymers, P0, P1b and P2b, indicating the aza-Michael addition was successful conducted.

The characteristic singles of aromatic rings of Azo and SA were not observed in FT-IR spectra due to their low molar contents (about 4.0 %). However, in the UV/vis spectra of P0a, P1b and P2b (Fig. 4), the characteristic absorptions at 324 nm of Azo^{66,67} and 311 nm of SA⁶⁸ chromophore were observed in P1b and P2b, respectively, further indicating the success of aza-Michael addition. Moreover, there was no absorption at the range of 550 to 750 nm; hence, 700 nm was reasonably selected for LCST measure.

As shown in Table 1 and Fig. 5A, the LCSTs of the prepared polysiloxanes in aqueous exhibited a strong dependence upon the content of incorporated Azo and SA groups. At a given content of NIPAs (about 30 %), the LCST of the as-prepared polysiloxanes decreased from 43.2 °C to 22.3 °C with increase of Azo from 0.0 % to 3.8 %, and from 43.2 °C to 12.4 °C with increase of SA from 0.0 % to 5.8 % respectively, because of the hydrophobic character of Azo and SA. Usually, the LCST of a thermo-responsive polymer may be adjusted in a wide range through the copolymerization of more hydrophobic or more





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or after (red line) irradiated by UV light of 365 nm for 0.5 h; (B) Δ LCST values of P1 (Δ) and P2 (\Box) after irradiated

hydrophilic monomers compared to the original main monomer. In addition, hydrophobic co-monomers that favour segment-segment interactions in polymers decrease the LCST.⁶⁹⁻⁷² For the same reason, when more NIPAAm was added from 30.3 % to 39.8 %, the LCST also decreased from 43.2 °C to 28.9 °C (POa and POb). Meanwhile, the as-prepared polysiloxanes cannot be dissolved in water even at 0 °C, when the amount of SA was increased up to 8.2 % or Azo up to 5.7 %.

The values of LCST of obtained polysiloxanes are also affected by UV light. As shown in Fig. 5B, in both Azo and SA modified polysiloxanes, higher LCST values were observed during irradiation with UV light. In a given content of NIPAs (30%), the LCST shift increased lineally from 0 °C to 3.4 °C and from 0 °C to 9.8 °C, with the increasing content of Azo from 0.0 % to 3.8 % and SA from 0.0 % to 5.8 % respectively. The LCST shift upon irradiation can be explained by the isomerization of Azo and SA. After irritation by UV light at 365 nm, Azo transforms from trans- to cis-configuration 73,74 and SA from the enol- to the keto-form 75,76 (Fig. 6), accompanied by an increase in dipole moment; and thus, an increased local polarity is present at the polymer backbone, which resulted in the increase of LCST. Analogous phenomenon has been reported in non-polysiloxane materials. Theato et al. immobilized Azo and SA onto glass, polycarbonate, and steel surface and the wettability of substrates surface could be



Fig. 6 Structural representation of isomerization of SA and Azo chromophore

switched reversibly by UV irradiation.77 Irradiation of Azo containing surfactants with UV-light with a wavelength of 360 nm resulted in more hydrophilic changes of the interfacial properties.⁷⁸⁻⁸⁰ Chen et al. embedded Azo into hyperbranched polyethylenimine terminated with isobutyramide and UVinduced trans-to-cis isomerization increases the local polarity of the supramolecular complexes, increasing LCST,^{81,82} Jochum et al. prepared series of Azo contained polyacrylamides or PNIPAAm, and higher LCST values were measured for UVirradiated solutions of the copolymers in comparison to the non-irradiated one.⁸²⁻⁸⁴ SA showed a change of color accompanied by a change in the dipole moment after irritation. An intramolecular proton-transfer reaction between the enol-imine and keto-amine forms. Jochum et al. reported LCST shift of up to 13 °C was found for poly(Ncyclopropylacrylamide) copolymer containing 15.0 mol % of AS groups.⁸⁵ However, the phase separation occurred at a broad range of temperatures. Compared with reported thermo- and light- dual responsive polymers, the obtained DRPSs were considered physiological inertness, non-toxicity, and biocompatibility, and exhibit high sensitive (the phase separation occurred within 0.3 °C) due to them flexible Si–O–Si backbones, which reduced conformational energy during them phase separation. Furthermore, the LCST values of DRPSs can be controllable by pH, salty and physic or chemical interaction with other hydrophobic/hydrophilic molecules. Accordingly, within the temperature range of the LCSTs before and after irradiation, an isothermal, light-induced precipitation of the polysiloxanes was possible.

Conclusions

In summary, we prepared two kinds of thermo- and photoresponsive polysiloxane containing different amounts of NIPAs and Azo/SA chromophores as side groups. The synthesis was based on a catalyst-free aza-Michael addition of PAPMS with NIPAAm and AAm-SA or AAm-Azo in a mild condition. The

ARTICLE

obtained DRPSs exhibited a LCST in aqueous solution, which depended strongly on the amount of incorporated Azo or SA chromophore. Furthermore, the UV-light induced isomerization of Azo or SA chromophore in the polymers, had an influence on the LCST. The LCST value was increased after irradiation, in which the difference between irradiated and non-irradiated ones was up to 9.8 °C when 5.8 % SA and 30 % NIPAs were attached onto the polysiloxane. Thus, in the temperature region between the LCST of non-irradiated and irradiated solutions, a light-controlled reversible solubility change was observed. In our approach, the NIPAs and chromophore were directly attached to the polysiloxane which opens the route to allow its combination with other immobilization chemistry. The approach may yield potential multifunctional and multi-responsive materials.

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A graphical and textual abstract for the contents pages

Graphical



Structure of thermo- and photo- dual-responsive polysiloxanes

Textual abstract

Two kinds of thermo- and photo- dual-responsive polysiloxanes were synthesized through a facile, effective, and catalyst-free aza-Michael addition.