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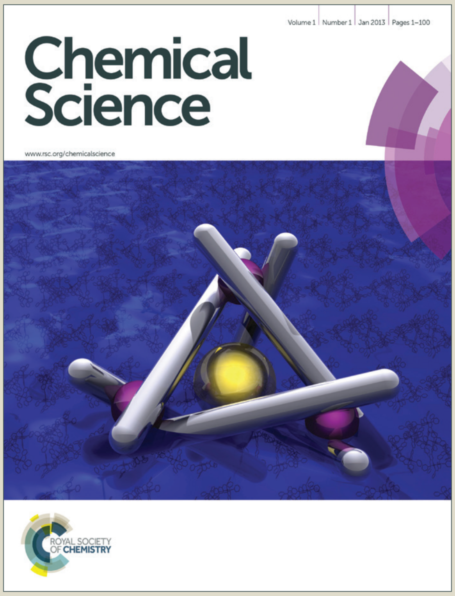

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemicalscience

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ultrafast and Reversible Thermochromism of Conjugated Polymer Material Based on Assembling of Peptide Amphiphiles†

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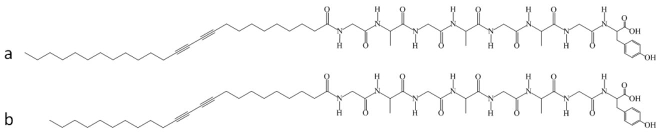
The translation of the colour change in chameleon to synthetic functional materials has attracted increasing interests, and conjugated polymers such as polydiacetylenes that undergo chromatic transitions under heating represent one of the most studied systems. However, they suffer a slow and irreversible colour change typically at low temperatures, e.g., 50-90 °C, which limits their sensing applications. In addition, they appear in powders or films and cannot satisfy the wearable electronics, a mainstream direction in sensing. Herein, the introduction of peptide to the side chain enables a continuous polydiacetylene fibre to exhibit ultrafast, reversible thermochromatic transitions at a high temperature of 200 °C. In particular, the reversible thermochromism occurs even at a temperature change rate of 5000 K/s, much higher than typically ~1 K/s of the other sensing polymers. The formation of a hierarchically assembled structure is responsible for this remarkable chromatism. In addition, a general and effective model is discovered to quantitatively predict the critical temperature of the colour change in polydiacetylene and guide the development of chromatic materials.

Introduction

Rapid and reversible colour transition in response to environmental changes is crucial to the survival of chameleons, which is also the goal of bio-inspired synthetic sensing materials.[1] One of the most widely investigated materials is conjugated polymers such as polydiacetylene (PDA) derivatives that exhibit obvious colour changes typically from blue to red under heating generally at a temperature range of 50-90 °C due to a decrease in the conjugation length of PDA backbone.[2, 3] The chromatic transition of PDA can be directly caught by the naked eyes, enabling a broad spectrum of optoelectronic and sensing applications.[4-9] However, on one hand, the available PDA materials often suffer slow response (tens of seconds to minutes), low reversibility (tens of cycles or even irreversible) and narrow working temperature range (less than 90 °C without introduction of inorganic components) and poor mechanical properties mainly due to relatively low structural regularity and strength of molecular interactions. Based on the same reasons, on the other hand, the available chromatic polymers have been generally made into powders or films, and it remains challenging to achieve continuous fibres that are required for the wearable electronics, a promising direction in sensing applications. To date, many strategies on designing thermochromatic PDA and other polymer materials had been attempted,[3] while it remains unavailable to overcome either of the above longstanding challenges.

Peptide-based supramolecular materials are widely studied for strong and directional interactions among subunits.[10-16] In this work, by incorporating the well-defined self-assembling performance of peptide-based amphiphiles, we present a general and efficient strategy to synthesize continuous thermochromatic PDA fibres besides uniform films and gels through an easy solution process. These polymer fibres are strong and exhibit a remarkably rapid response even at a high temperature up to 200 °C. In addition, the critical temperature on the thermochromatic transition can be well tuned by varying the length of alkyl chains. An effective model that can quantitatively predict the critical temperature, for the first time, is further developed for chromatic polymers.



Scheme 1 Peptide amphiphile molecules used in this study. a) C_{25}-GAGAGAGY. b) C_{23}-GAGAGAGY.

Experimental

Preparation of PAs

Peptide GAGAGAGY was prepared as reported in our previous work.[17] 10,12-pentacosadiynoic acid (0.24 mmol) was dissolved in DMF (20 mL). After addition of O-(Benzotriazol-

1-yl)-N,N,N',N'-tetramethyluronium tetrafluoroborate (0.24 mmol) and diisopropylethylamine (0.24 mmol), the solution was stirred at room temperature for 30 min to activate the carboxyl group of 10,12-pentacosadiynoic acid. Then GAGAGAGY (0.20 mmol) dissolved in 10 mL DMF was added dropwise to the solution. After 3 h at 0 ^{o}C the DMF was removed in vacuum and the residual solid was dissolved in NaOH (10 mL 0.1 M). The solution was acidified by HCl for solids to separate out. The solids were washed with water and lyophilized. C_{25}-GAGAGAGY was characterized by liquid chromatography-Electrospray ionization mass spectrometry (LC/ESI-MS) (m/z = 979.88, expected 979.87 [M+H]$^+$), MALDI-TOF (m/z = 1023.88, expected 1023.83 [M+2Na-H]$^+$) and ^{1}HNMR [400 MHz, DMSO-d_6, ppm]: δ 0.82 (t, 3H), 1.10-1.49 (m, 41H), 2.07 (t, 2H), 2.23 (t, 3H), 2.76 (m, 2H), 3.67 (m, 8H), 4.24 (m, 4H), 6.61 (d, 2H), 6.95 (d, 2H), 7.96 (m, 8H), 9.17 (s, 1H). C_{23}-GAGAGAGY was prepared and characterized analogously, using peptide GAGAGAGY and 10,12-tricosadiynoic acid. LC/ESI-MS (m/z = 951.38, expected 951.83 [M+H]$^+$), MALDI-TOF (m/z = 995.79, expected 995.79 [M+2Na-H]$^+$) and ^{1}HNMR [400 MHz, DMSO-d_6, ppm]: δ 0.82 (t, 3H), 1.05-1.49 (m, 37H), 2.05 (t, 2H), 2.24 (t, 3H), 2.76 (m, 2H), 3.67 (m, 8H), 4.21 (m, 4H), 6.60 (d, 2H), 6.95 (d, 2H), 8.02 (m, 8H), 9.15 (s, 1H).

Preparation of fibres, membranes and gels

C_{25}-GAGAGAGY/C_{23}-GAGAGAGY (0.050 mmol) was dissolved in NaOH (5 mL 0.01 M) before adjusting pH to 7 by concentrated hydrochloric acid. The solution was heated to 60 ^{o}C to dissolve the solid and then cooled to room temperature slowly. A colourless or light red gel fibre was obtained by injecting the solution into HCl (0.1 M) with a 1 mL syringe. After illumination with UV light (WFH-204B, 254 nm) at a distance of 5 cm for 3 min, a blue PA-PDA fibre was obtained. Membranes were prepared by coating on glass slide and bulk gels were prepared by molding in plastic moulds. These were irradiated in the same way as the fibres. Fibres and membranes were dried in air before heat test.

Measurements

UV-Vis. The membranes were measured on a SHIMADZU UV-2550 with temperature controlling accessories. Membranes were placed on a quartz cuvette and equilibrated at each temperature for 3 min. FE-SEM. Gel fibres and membranes were frozen by liquid nitrogen before freeze-drying, and sputtered with gold before imaged on a Hitachi S-4800 FE-SEM, operated at 1.0 kV. FT-IR. Transmission FTIR absorption spectra were collected on a Nicolet Nexus-470 spectrometer with PA-PDA membranes between KBr plates. Samples were equilibrated at each temperature for 3 min before scanning for 64 times. XRD. The X-ray scans of PA-PDA materials was performed with a D8 Discovery (Bruker) diffractometer, on a 16407 high-temperature stage. The X-ray source was Cu Kα radiation (λ = 1.5418 Å), at 40 mA and 40 kV. The heating rate was 5 ^{o}C/min, and the sample was stabilized for 1 min at each temperature before measurement. Raman spectra. Raman spectra were recorded on a Renishaw inVia reflex Raman Spectrometer, with a 785 nm semiconductor laser and scanned 4 times after equilibration for 3 min at each temperature. TGA. Thermogravimetry analysis was performed on a Pyris-1 thermo gravimetric analyzer, with a heating rate of 10 ^{o}C per minute from 30 ^{o}C to 600 ^{o}C, in air. DSC. DSC was performed on a TA Q2000 instrument, with a heating rate of 10 ^{o}C per minute and cooling rate of 20 ^{o}C per minute going from 20 ^{o}C to 100 ^{o}C. Flash DSC. Flash DSC was performed on a fast scanning calorimeter (Flash DSC 1, Mettler Toledo), with a heating rate and cooling rate stated in the main text. In flash DSC analysis, silicone oil was used to fit the samples on the stage.

Results and discussion

Thermochromism and mechanical properties

The octapeptide, GAGAGAGY, originally obtained from hydrolyzed Bombyx mori silk fibroin,[17] was coupled with 10,12-pentacosadiynoic acid to yield the peptide-based amphiphilic (PA) diacetylene, i.e., C_{25}-GAGAGAGY (Scheme 1a). As expected, the C_{25}-GAGAGAGY self-assembled into nanoribbons that further aggregated into bundles in a parallel fashion at a pH around 7 in aqueous solution (1 wt%).[18] When the pH was decreased, the solution gelled and could be then made into various shapes such as fibres (Fig. 1a, b), membranes (Fig. 1c) and bulk gels (Fig. 1d), depending on the used methods of extrusion, coating and molding, respectively. At the same time, the conjugated triple bonds within the assembly fulfill the topological conditions for the reaction and can be photo-polymerized rapidly to form peptide-based amphiphilic polydiacetylene (PA-PDA) under UV light. The resulting material, interestingly, consisted of nanofibrillar microstructures, as observed by field emission scanning electron microscopy (FESEM) (Fig. 2a, b). For the convenience in exploring the structure and theromchromatic property in PA-PDA, both films and gels are also carefully investigated besides fibres.

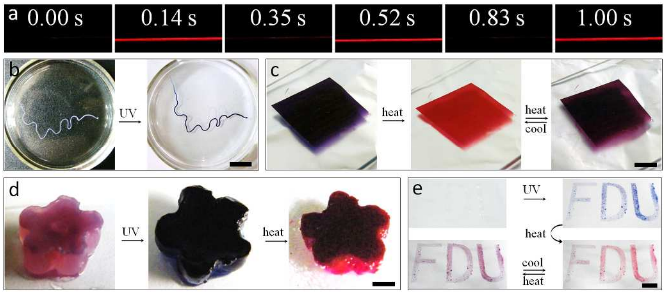


Fig. 1 Thermochromism of PA-PDA materials. a) Screenshots of PA-PDA fibre within 1 second upon heating and cooling. b) The light red fibre obtained through extruding turns blue under UV. c) PA-PDA membranes (dried, left to right): at room temperature, at 80 ^{o}C, after cooling to room temperature. d) (Left to right) PA hydrogel, PA-PDA hydrogel, heating at 80 ^{o}C. e) (Clockwise) PA hydrogel (0.2 wt %) sprayed into pattern, after UV irradiation, thermochromatic behavior of sprayed pattern. The length of the fibre in a) is 1 cm. The bars represent b) 1 cm, c) 2 cm, d) 1 cm, e) 3 cm

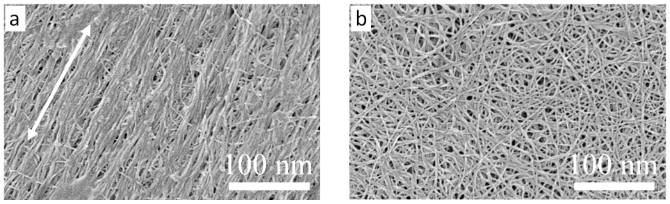


Fig. 2 FE-SEM images of PA-PDA fibre a) and membrane b). The nanoribbon bundles highly oriented in the shear direction (white arrow) in fibre and distributed randomly in membrane.

These materials displayed noteworthy mechanical properties, illustrated by a tensile modulus of 3 GPa for the fibres and a compression modulus of 10 kPa for the gels (Fig. S1 Supplementary Information, SI). It is worthwhile to note that the modulus of fibre is at the same order of magnitude with generic elastic modulus of glassy polymers,[19] showing a promising prospect for the wearable electronic devices. The PA-PDA fibre exhibited an ultrafast, reversible thermochromism. At least 3 chromatic transition cycles could be completed in 1 second upon heating and cooling (Fig. 1a, Video S1). Such a rapid thermochromism has not been previously observed for PDA and other sensing polymers. The rapid thermochromism was also observed in the PA-PDA film and gel. As an application demonstration, PA-PDA hydrogels were sprayed into a pattern for a reversible chromatic transition under heating (Fig. 1e).

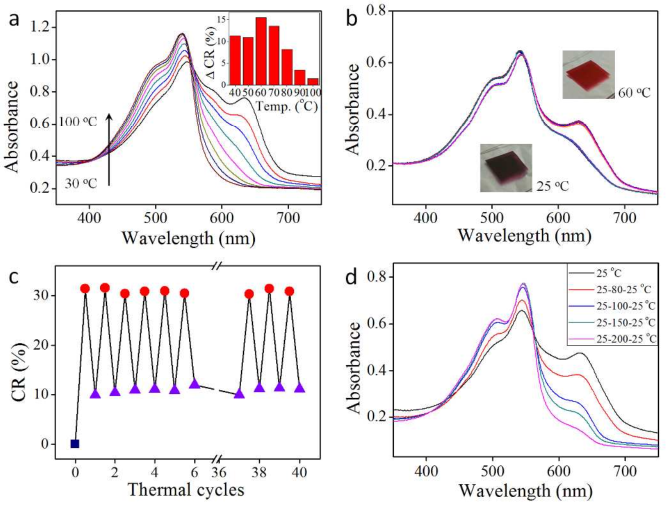


Fig. 3 UV-Vis characterization to the thermochromism of PA-PDA materials. a) UV-Vis spectra of PDA membranes at 30～100 °C (inserted, ΔCR values at increasing temperatures. b) UV-Vis spectra of 25 °C and 60 °C cycles. c) CR values of scores of thermal cycles between 25 °C and 60 °C. d) UV-Vis spectra of PDA membranes which were heated to 80 °C, 100 °C, 150 °C, 200 °C before cooling to 25 °C, respectively.

To further investigate the chromatic transition, the optical properties of the PA-PDA films at various temperatures were characterized by UV-vis spectroscopy. The peak at 630 nm was associated with a blue phase and the peak at 540 nm corresponded to the red phase (Fig. 3a). The peak intensity at 630 nm was decreased while the one at 540 nm was increased with the increasing temperature, which was also verified by the colour change from blue to red. When the temperature was decreased, the UV-vis spectrum was recovered to a large extent after the first cycle and reached an equilibrium from the second cycle (Fig. 3b), while the rapid reversibility was maintained even after dozens of thermal cycles (Fig. 3c, CR,[20] $(B_0-B_{temperature})/B_0\times100\%$, $B_{temperature}=A_{630}/(A_{630}+A_{540})$ and B_0 means initial value, $A_{wavelength}$ is absorbance at the corresponding wavelength). Furthermore, different heating temperatures corresponded to different recovered spectra which, in our opinion, is due to a partly irreversible conformational transition in the first heating stage (Fig. 3d). Nevertheless, the PA-PDA materials showed a reversible thermochromism even at a high temperature of 200 °C (Fig. S2, video S2), much higher than those below 90 °C in the other PDA systems. It is even much higher than 145 °C in the PDA/silica composite.[21]

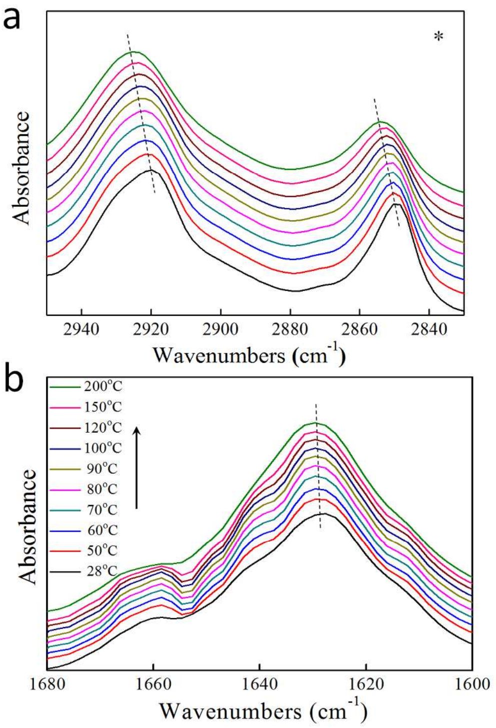


Fig. 4 FTIR spectra of PA-PDA membranes at different temperatures. a) share the legend with b).

Structural characterization and mechanism

Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy were used to investigate the structural transformation during heating. Fig. 4a and 4b compare the FTIR spectra of a PA-PDA film at different temperatures. The $\nu_{as}(CH_2)$ (2920 cm^{-1}) and $\nu_s(CH_2)$ (2850 cm^{-1}) vibration were shifted to higher frequencies, suggesting a more disordered conformation of PDA segments.[22] However, the peak at 1628 cm^{-1} ascribed to a peptide β-sheet showed hardly any shift, indicating the β-sheets formed by the PA segment were stable during heating. This conclusion was also verified by XRD at different temperatures (Fig. 5a). The peaks at 2θ of 20° (4.4 Å) that corresponds to the hydrogen bond spacing of β-sheet structure[23] were nearly stable and only shifted a little at 200 °C, while the peak at 2θ of 23° (3.9 Å) that is attributed to the lattice of alkyl chains[24] was obviously shifted and vanished with increasing temperatures. On the other hand, the Raman spectra (Fig. 5b) illustrated that C=C and C≡C undergo a conformational transition during the heating process, as can be deduced from the shift of the peaks at 1454 cm^{-1} and 2086 cm^{-1} at room temperature to 1513 cm^{-1} and 2117 cm^{-1} at high temperature, respectively.[7, 25] Obviously, the higher wavenumber corresponds to higher energy of the conjugated C=C and C≡C and stronger absorption at lower wavelength peak in UV-Vis spectrum, with the material showing red colour. In addition, the Raman spectra from 30 to 80 °C also corroborated that the conformational transitions of C=C or C≡C were reversible (Fig. S3, SI). The FTIR spectra in combination with XRD and Raman spectra demonstrated that the two segments of the molecule behaved differently upon heating: the peptide segment was stable without obvious conformational transition or thermal degradation (Fig. S4, SI), while the conjugated double and triple bonds containing alkyl chain segment experienced a reversible conformational transition.

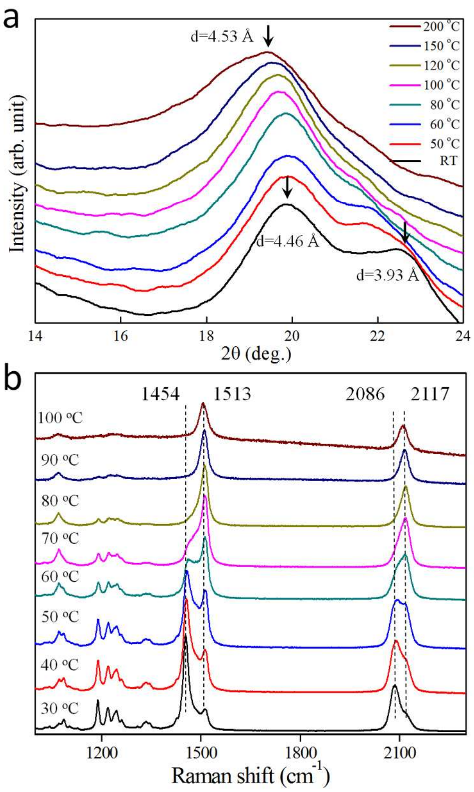


Fig. 5 a) X-ray diffraction analysis of PA-PDA at different temperatures. b) Raman spectra of PA-PDA membranes at different temperatures.

Therefore, it can be concluded that the double and triple bonds were changed from all-trans configurations to partly-cis configurations as the mobility of the alkyl chains was increased during heating. Different from the other studies,[26] the β-sheets of peptide side chains restricted the disorder and the molecular separation remained stable under heating at high temperatures, which drove the PDA backbone back to its original co-planar configuration upon cooling. At the first heating cycle, the partly unstable structures were disrupted and cannot be recovered completely, resulting in a partial recovery after the first cycle.

Transition temperature investigation and modelling

DSC was employed to study the transition temperature of the PA-PDA materials to gain more insight into the thermochromatic behavior resulting from the thermal motion of the alkyl chain. Only one endothermic peak was observed at about 60 °C at the temperature range of -80 to 200 °C (Fig. S5, SI), which can be attributed to the mobility of the alkyl chain and corresponded to the thermochromatic transition.[27] The critical temperature was further verified by the Raman spectra where two main shifts from 1454 to 1513 $\mathrm{cm^{-1}}$ and 2086 to 2117 $\mathrm{cm^{-1}}$ occurred at around 60 °C. In addition, the maximal ΔCR also appeared at 60 °C (inserted, Fig. 3a). Furthermore, although the endothermic peak was weaker at the second cycle, it can be completely repeated with a significant chromatic memory (Fig. 6a). To illustrate the rapid colour change, a fast scanning calorimeter (Flash DSC)[28] with a high temperature change rate of 5000 K/s was employed to further explore the chromatic transition of PA-PDA. Interestingly, the endothermic peak was still present (Fig. 6b), indicating that the reversible thermochromism occurred even at a temperature change rate of 5000 K/s, compared with typically ~1 K/s in the previous reports.[21]

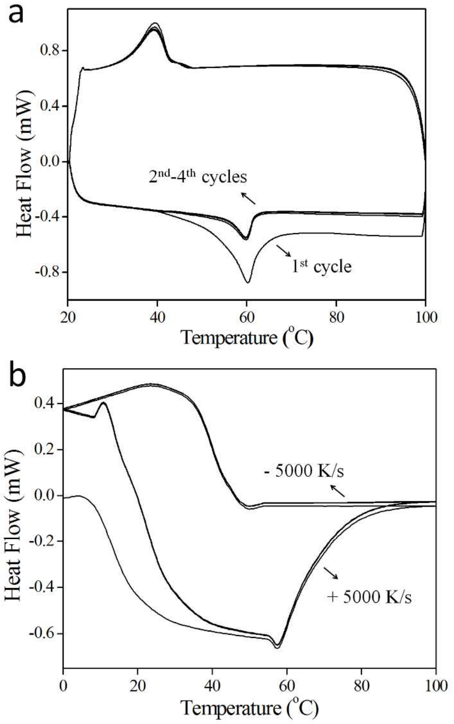


Fig. 6 a) DSC analysis of PA-PDA. Only one endothermic peak at 60 °C appeared in heating progress from 20 °C to 100 °C and the endothermic peaks completely repeated from the second cycle. b) Flash-DSC analysis of PA-PDA at heating and cooling rates 5000 K/s, with endothermic peaks still appearing.

Inspired by the idea that the thermochromism is induced by increased mobility of alkyl chains, whose transition temperature should be length dependent, we reasoned that the colour transition temperature could be changed by varying the alkyl chain length. To this purpose, a similar PA 2, C_{23}-GAGAGAGY (Scheme 1b), with two carbon atoms less than C_{25}-GAGAGAGY was synthesized and employed to prepare the corresponding PA-PDA. Unsurprisingly, the material displayed similar thermochromatic behavior, but the DSC result (Fig. S6, SI) showed that the transition temperature was about 52 °C, which is 8 °C lower than that of C_{25}-GAGAGAGY PA-PDA. Given that the transition temperatures of the strongly bonded peptide chain segments in the structure would be expected to be far higher, we tested the hypothesis that the transition is due to the onset of increased motion in the alkyl segments of the short hydrocarbon chain from a stacked crystal structure to a more disordered rubberlike state above a crystal melting temperature, T_m.

To do this, we used the method of Group Interaction Modelling, which is described in detail elsewhere.[29] The energetic condition for the crystal melt and glass transitions (E_t) is quantified by the Born elastic instability condition as a defined fraction 0.213 of the cohesive binding energy (E_{coh}) of interacting segments of a polymer chain in a Lennard-Jones potential energy well. The energy to attain this condition is provided by the zero point energy (H_c) and the thermal energy of molecular segment vibrations (H_T). For the crystal state, $H_c = 0.04\ E_{coh}$. Thermal energy is approximated from the full Debye theory for one dimensional skeletal mode vibrations in terms of the parameters of degrees of freedom per group (N), the molar gas constant (R = 8.3 J/mol/K) and the reference temperature (θ).

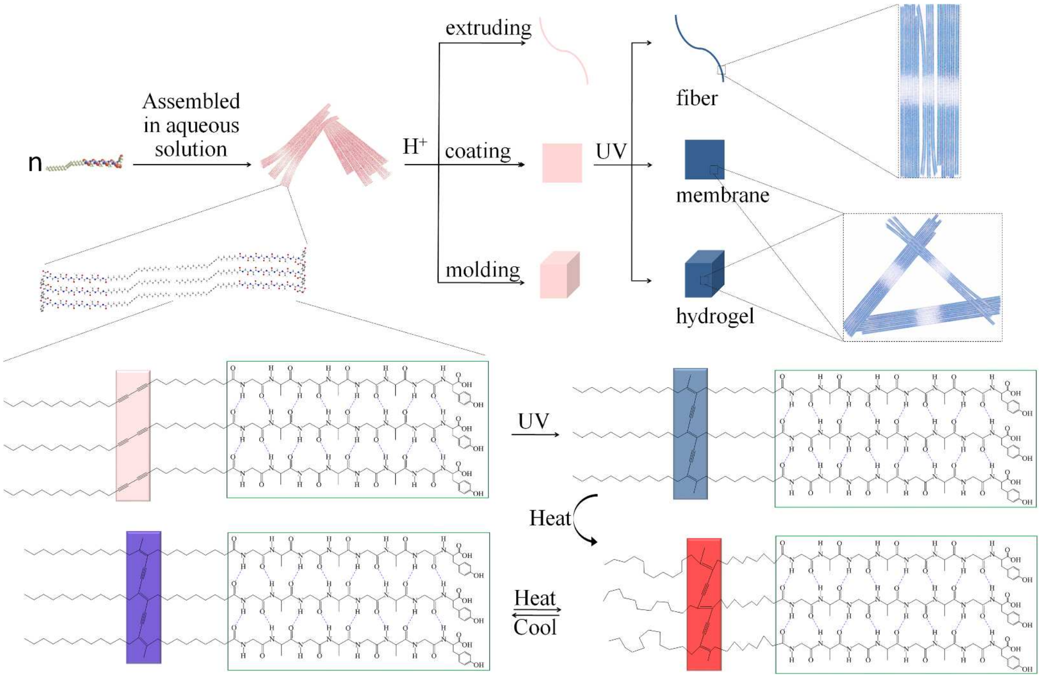
$$E_t = 0.213\ E_{coh} = H_c + H_T = 0.04\ E_{coh} + \frac{N'\ R}{3}\left(T_m - \frac{\theta}{6.7}\tan^{-1}\left[\frac{6.7T_m}{\theta}\right]\right)$$

Taking a simple characteristic CH_2 group for the potentially mobile segment, an infinite chain would have N = 1 normal modes for tight crystal packing, E_{coh} = 4500 J/mol from group additivity tables, and θ = 550 K. However, the short chains in the model structure need to be adjusted for structural features: the free chain end needs six extra degrees of freedom and the crosslinked end eliminates three degrees of freedom due to restrictions on motion. So for a chain of n atoms, the adjusted degrees of freedom become N'=N (1+3/nN). For C_{23}-GAGAGAGY and C_{25}-GAGAGAGY, n = 10 and n = 12, respectively, since that is the number of CH_2 groups in the terminal segment beyond the crosslink sites. Thus, the transition temperature can be calculated by solving the simplified energy relation with the specified parameter values:

$$\frac{281}{1+\frac{3}{n}} = \left(T_m - \frac{\theta}{6.7}\tan^{-1}\left[\frac{6.7T_m}{\theta}\right]\right)$$

We predict T_m = 52 °C and 61 °C for n = 10 and n = 12 respectively, which are in good agreement with the observations of the transition temperatures, i.e. 52 °C and 60 °C by DSC. The result also verifies the hypothesis that the reversible transition is due to the onset of increased motion in the alkyl segments, with stable peptide segments. Moreover, the modelling equation may be extend to the other sensing polymers based on alkyl side chains, encouraging us to investigate further and may shed a light on designing a series of fast colorimetric detection and sensing systems.

As a control experiment, the PDA materials obtained from C_{25} and C_{23} precursors without GAGAGAGY at the side chain cannot be made into continuous fibres; the PDA films or powders exhibited a thermochromatic transition at a low temperature range of 50 to 80 °C; the colour change from blue to red was slow (typically tens of seconds), and the chromatic transition was not reversible. Therefore, the formation of peptide-based amphiphiles is a key to the extraordinary thermochromatic properties of PA-PDA materials.



Scheme 2 Self-assembly and subsequent polymerization of PA and thermochromism of PA-PDA.

Conclusions

In summary, a continuous PDA fibre has been developed to exhibit ultrafast, reversible thermochromatic transitions at an unusual high temperature of 200 °C by designing peptide-based amphiphilic precursors (Scheme 2). At least 3 thermochromatic cycles could be completed in 1 second, compared with tens of seconds to minutes for 1 thermochromatic cycle in the other polymers, and the reversible thermochromism occurs even at a temperature change rate of 5000 K/s, much higher than typically ~1 K/s in the other sensing polymers. The formation of a hierarchically assembled structure is responsible for the remarkable chromatism. In addition, a general and effective model is further concluded to quantitatively predict the critical temperature of the chromatic transition and guide the advancement of chromatic materials. Therefore, this work also presents an efficient paradigm in the development of high-performance sensing polymer materials by incorporating peptide-based side chains for hierarchical structures.

Acknowledgements

This work was supported by National Natural Science Foundation of China (NSFC 21034003), Program of Shanghai

Subject Chief Scientist (12XD1401000). The authors thank Prof. Wenbing Hu and Zhaolei Li (Nanjing University, China) for performing Flash DSC experiment.

Notes and references

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†Electronic Supplementary Information (ESI) available: mechanical properties of materials, pictures of membranes at high temperature, Raman spectra at varying temperatures, thermogravimetry analysis, DSC results and videos. See DOI: 10.1039/b000000x/

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