Aggregation-Induced Reversible Thermochromism of Novel Azo Chromophore-Functionalized Polydiacetylene Cylindrical Micelles

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Received July 29, 2008; Revised Manuscript Received October 17, 2008

ABSTRACT: We demonstrate a new strategy for improved stabilization of polydiacetylene micelles. They show temperature-induced color changes, which are fully reversible even at varying pH. A novel azo chromophore-functionalized amphiphilic diacetylene molecule is synthesized and used to prepare self-assembled cylindrical micelles. The micelles can be polymerized by 254 nm light irradiation. The azo chromophores form H- and J-like aggregates in the polydiacetylene micelles and increase the stability of the micelles, which leads to fully reversible thermochromism of the micelles in the temperature range between 20 and 90 °C and the pH range between 5.6 and 9.6.

Introduction

Polydiacetylenes (PDAs) are well-known for their stimuli-responsive blue to red color change,[1−4] which depends on temperature,[1,4,5] pH,[6] stress,[7] ions,[8] solvent,[1,9] and biologic ligand interactions.[2,10] The color change can be easily perceived by the naked eye. Therefore, this unique property of PDAs is attractive for applications as chemosensors,[3,11] biosensors,[2,10] ion sensors,[12] and molecular switches.[13] In many cases, the color change of PDAs is irreversible. This is a drawback for their applications as sensors and "on−off−on" switches. To achieve *reversible* color changes, modifications of diacetylene monomers have been pursued. For example, multiple hydrogen bonding,[14−20] both hydrogen bonding and strong aromatic interactions,[14,15,21] ionic interations,[22] and covalent bonds[23,24] were introduced into diacetylenes to enhance the bonding among the substituent groups in side chains. The most popular and useful methods reported are hydrogen bonding and covalent bonds. Recently, it was demonstrated that the reversible thermochromism of PDAs occurs in thin films by the covalent bond interactions among the substituent groups of PDAs.[23,24] Furthermore, it was also demonstrated that the network of multiple hydrogen bonding can induce reversible color changes of PDAs in both thin films and vesicles or micelles dispersed in solvents.[14−20]

However, micelles stabilized by hydrogen bonding suffer from poor stability at high pH values. It is well-known that the pH will affect the hydrogen-bond formation. In principle, the network of hydrogen bonding among substituent groups will be lost at high pH so that the reversible color changes of these PDAs will become irreversible. The specific sensor action of PDAs is sometimes hindered by the multiple responses of PDAs to many stimuli. It is a challenge to obtain a sensor system, for example, which responds to temperature only but is independent of pH. Therefore, it would be highly desirable to get an alternate stabilization method of PDA vesicles or micelles with reversible color changing property, which is useful in a broader range of pH.

The aim of our work is to fabricate a pH stable PDA which enables reversible color changes and provide platforms for specific sensing and molecular switches. H- or J-like aggregation is a kind of supermolecular interaction, which forms among close-packed chromophores.[25,26] As compared with hydrogen bonding, the stabilization by aggregation is not so sensitive to pH. The aggregation properties of azo chromophores are widely studied. They can easily form H- or J-like aggregation in thin films, vesicles, or micelles.[27−36] Here, we report on the design and synthesis of a novel azo chromophore-functionalized diacetylene and demonstrate that aggregation of the azo chromophores improves the pH stability of the PDA micelles and enables reversible thermochromism of the PDA.

Experimental Section

The chemical structure of the new azo chromophore-functionalized diacetylene molecule ((*E*)-4-((4-(tricosa-10,12-diynoyloxy)-phenyl)diazenyl)benzoic acid, short for AzoDA) is shown in Figure 1. The synthesis of AzoDA is described in the Supporting Information. The chemical structure is fully characterized by ^{1}H NMR, FTIR, and mass spectrometry.

Preparation of the micelles: 2 mg of AzoDA was dissolved into 2 mL of THF in a flask. The solvent was removed by a stream of N_2 gas, and then the flask was vacuum pumped for about 4 h to remove residual organic solvent. After that, 6 mL of a buffer solution (HEPES, 5 mM) was added into the flask to hydrate the dry materials. The sample was sonicated at 80 °C for 30 min. The resulting emulsion is cooled at 4 °C overnight. Polymerization was carried out at room temperature by irradiating the emulsion at 254 nm with an ordinary UV-hand lamp. The micelle emulsion was filtered through a 5 μm filter before measurements. Normally, the sample is diluted to 1/6 concentration by Milli-Q water before UV−vis absorption spectra measurement. The pH is about 5.6 at room temperature.

UV−vis absorption spectra were measured on a Perkin-Elmer Lambda 900 spectrometer, which was also equipped with a Perkin-Elmer temperature control system. Scanning electron microscopy (SEM) images of polyAzoDA micelles were obtained on a LEO Gemini 1530 system. Atomic force microscopy (AFM) images of polyAzoPDA micelles were obtained on a Dimension 3100 system. The samples for SEM and AFM were prepared by applying a drop of the original high-concentration micelle emulsion onto a clean silicon wafer surface and leaving it dry in air overnight. Isolated micelles were prepared by spin-coating a diluted emulsion on a clean silicon wafer.

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10.1021/ma801709n CCC: $40.75
Published on Web 12/08/2008

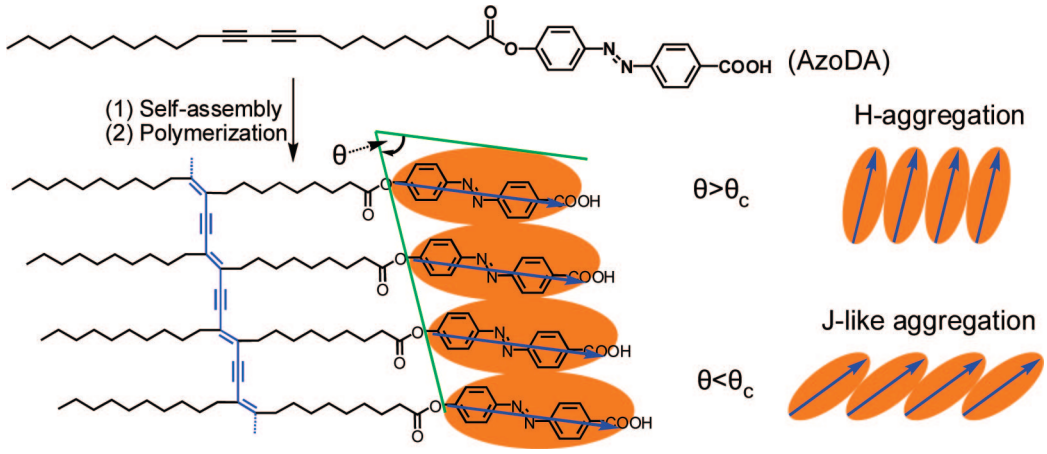

Figure 1. Chemical structure of AzoDA and model of the H- and J-like aggregates in polyAzoDA. The type of aggregation refers to the angle θ between the coplanar transition dipoles and their interconnecting axis.

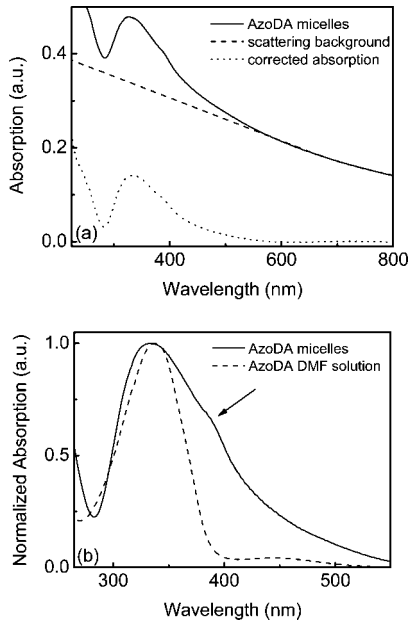

Figure 2. UV−vis absorption spectra of AzoDA. (a) AzoDA micelles in water (full line), scattering background fitted to the micelle absorbance in the range 600 nm < λ < 800 nm using eq 1 and extrapolated to the shorter wavelengths (dashed line) and absorption spectrum of AzoDA micelles in water after subtraction of scattering background (dotted line). (b) Comparison of normalized absorption of AzoDA micelles in water after subtraction of scattering background (full line) and AzoDA in DMF (dashed line). The arrow points at the shoulder in the absorption of AzoDA micelles which indicates J-like aggregates.

Results and Discussion

The micelles of the amphiphilic AzoDA molecules were prepared as described above. The absorption spectrum of the AzoDA micelles in water is shown in Figure 2a. The micelles show light scattering, which causes an apparent tail in the absorption spectrum. The scattering background of the micelles at $\lambda > 600$ nm can be fitted well by an empirical law of the form[37]

$$\alpha_{\text{scattering}} = A + B/\lambda^2 + D/\lambda^4 \qquad (1)$$

where A is the contribution of large particle scattering, B is the contribution of the inhomogeneities on the order of λ in size (Mie scattering), and D is the contribution of inhomogeneities much smaller than λ (Rayleigh scattering).

If the scattering background spectrum is subtracted from the measured spectrum, we obtain the corrected absorption spectrum of the micelles, which is also shown in Figure 2a. This intrinsic absorption spectrum of AzoDA micelles is compared with the absorption spectrum of AzoDA dissolved in DMF and shown in Figure 2b. There are two important differences in the absorption spectra between the solution of AzoDA in DMF and the micelles of AzoDA in water. One is that the $\pi-\pi^*$ absorption peaks of the micelles and DMF solution are at 333 and 337 nm, respectively. The absorption peak of the micelles is slightly blue-shifted. The main difference is that the absorption band of the micelles becomes much broader. The blue shift cannot be caused by differences of polarity between DMF and H_2O, since the polarity of H_2O is even bigger than that of DMF. If AzoDA could form a real solution in H_2O, the $\pi-\pi^*$ absorption wavelength at the peak should be red-shifted compared with the DMF solution.

We explain the absorption spectrum of the AzoDA micelles with aggregations of the azo chromophores.[26−36] The type of aggregation refers to the angle between the coplanar transition dipoles and their interconnecting axis as shown in Figure 1. There is a critical angle $\theta_c = 54.7°$. Two cases are distinguished. Azo chromophores form so-called H-aggregates if $\theta > \theta_c$ and so-called J-like aggregates if $\theta < \theta_c$.[27−36] As compared to the isolated chromophore, the absorption bands of H-aggregates are blue-shifted and the J-like aggregates are red-shifted.

The blue shift in the $\pi-\pi^*$ absorption indicates an increase in population for azobenzene groups in the H-aggregated state. It is a well-known phenomenon that azobenzene groups form H-aggregates in thin films as well as in vesicles or micelles.[27−36] The full widths at half-maximum of the $\pi-\pi^*$ absorption bands are 105 nm for the micelles and 67 nm for the solution. Detailed inspection of the micelle absorption spectrum shown in Figure 2b reveals a shoulder at around 390 nm, which is not present in the AzoDA absorption in DMF. This indicates an additional red-shifted band compatible with J-like aggregates.[27,29,31,34,36] This result indicates that not only H-aggregates but also J-like aggregates appear in AzoDA micelles, which is in accordance with reports of other groups.[27,29,31,34,36] We conclude that our AzoDA micelles contain both H- and J-like aggregates with widely varying angles θ, which are responsible for the broadening of the spectrum in the near-UV range.

The trans−cis photoisomerization of azobenzene groups is well-known.[38] It was frequently pointed out that aggregation can strongly hinder the photoisomerization of azobenzene groups.[32−34,36,39] The formation of aggregation in the micelles is in line with the absence of photoisomerization in AzoDA micelles. We verified that AzoDA can be easily isomerized by

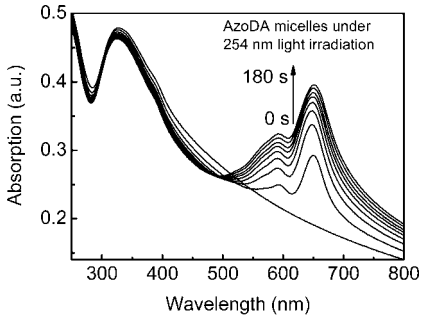

Figure 3. UV−vis absorption spectra of AzoDA micelles after subsequent irradiations by 254 nm light inducing the polydiacetylene absorption band at around 647 nm.

the irradiation of UV light and visible light in DMF solution. AzoDA micelles in water, on the other hand, did not show any detectable change in the absorption spectrum after 10 min irradiation by 365 nm UV light provided by a high-pressure mercury arc combined with water and UG11 filters. The photoisomerization behavior of azobenzene groups is obviously inhibited by the aggregation in the micelles. The absence of the photoisomerization in the micelles indicates that the aggregation in the AzoDA micelles is very strong as reported earlier.[32]

Aggregation can occur only when the chromophores can approach each other in space.[26,33] The photopolymerization of diacetylene also needs a close-packed structure because the mechanism of photopolymerization of diacetylene is a topochemical reaction.[40] The polymerization happens in close-packed structures, such as crystals,[40] monolayer,[41,42] Langmuir−Blodgett films,[43,44] liposomes,[45] micelles, or vesicles.[45] AzoDA micelles can be polymerized by the irradiation of UV light at 254 nm as shown in Figure 3. The characteristic absorption band of PDA appears at around 647 nm. This result indicates that AzoDA is in a densely packed environment and polymerized micelles are formed, called polyAzoDA micelle. This kind of structure is compatible with aggregation of azo chromophores.[26,33] Figure 1 shows the model of the aggregation in the polyAzoDA micelle.

We also designed another experiment to study the aggregate properties of polyAzoDA micelles. After polymerization, the micelles become stable to the addition of some organic solvents. We added DMSO to the micelles and measured the absorption spectra of polyAzoDA micelles in the mixture of water/DMSO. The $\pi-\pi^*$ absorption band gradually becomes narrow as the content of DMSO increases. The photoisomerization of azo chromophores in polyAzoDA can also take place as the organic solvent is added. This result indicates that the aggregates of azo chromophores are destroyed by adding the organic solvent. This experiment confirms again that azo chromophores in polyAzoDA micelles in water must be in a strong aggregation state.

The morphology of the polyAzoDA micelles is observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The samples for SEM and AFM measurements were prepared by casting micelle emulsions on silicon wafers as described in the Experimental Section. The SEM images in Figure 4a,b show that polyAzoDA micelles have a preferred cylindrical shape; i.e., they appear as rodlike micelles. The morphology of the cylindrical micelles is further confirmed by AFM images shown in Figure 4c for comparison. In Figure 4c, the morphology of the micelles is similar to that in Figure 4a,b. Isolated micelles can be obtained by spin-coating, and the morphology of the isolated micelles is shown in Figure 4d, which provides further evidence that the micelles have preferred cylindrical shapes. Usually, the cylindrical micelles are large and polydisperse.[46] From the SEM images, we can see that the size range of polyAzoDA micelles is between <100 nm and several micrometers.

These cylindrical micelles can be formed when the critical packing parameter v/a_0l_c of the amphiphilic molecule is between 1/2 and 1/3,[46,47] where v is the volume of the hydrocarbon chain, a_0 is the optimal area of the hydrophilic group and l_c is the critical chain length of the hydrophobic group. The formation of the special cylindrical micelles is probably due to the aggregation properties of azo chromophores. Usually, cylindrical micelles are formed by single-chained lipids with small head-group areas.[46] The optimal head-group area a_0 is affected by two factors. One is attractive hydrophobic interactions of the hydrocarbon chain, which will decrease a_0, and the other is the repulsive interaction between the polar head groups, which will increase a_0.[46] In our case, besides the normal hydrophobic interactions of the hydrocarbon chain, there is H- and J-like aggregation among azobenzene groups, which provides an additional attractive interaction. So, the optimal area a_0 of the hydrophilic group becomes even smaller and cylindrical micelles are formed.

Figure 5 shows the UV−vis absorption spectra of polyAzoDA at different pH. As expected, polyAzoDA shows good pH stability. The absorption band at around 650 nm does not shift in a broad pH range, and the color of the micelle emulsion keeps blue as the pH changes. In earlier reports, varying pH always induced reversible or irreversible color changes of PDAs.[6,14,18] The pH stability of polyAzoDA micelles presented here is unique and different from the other PDAs.[6,14,18] This absence of pH sensitivity demonstrates that our design of aggregation enforced polyAzoDA micelles successfully improves their stability.

Our aggregation stabilized polyAzoDA micelles enable fully reversible thermochromism. Figure 6 shows the temperature-dependent UV−vis absorption spectra of polyAzoDA micelles during heating and cooling. The wavelengths of the absorption peaks of polyAzoDA micelles during the heating and cooling processes are shown in Figure 7. The absorption peak of PDA in polyAzoDA micelles is at around 647 nm at room temperature. During the heating process, the absorption peak is gradually blue-shifted, and the color of the micelles changes accordingly. At 85 °C, the absorption peak reaches 575 nm. During the cooling process, the absorption peak is reversibly red-shifted. Correspondingly, the color also changes reversibly back to blue. We conclude that the thermochromism of polyAzoDA micelles is fully reversible. The reversible thermochromism can be easily observed by naked eye.

The underlying mechanisms for the reversibility of the thermochromism are based on two stabilization processes: (i) the well-known polymerization of diacetylenes induces improved stability of PDA micelles[14−24] and (ii) the aggregation of azo chromophores, which provides a more rigid morphology. However, the stabilization by polymerized PDA micelles alone is not sufficient. To prove this, we performed the following two control experiments.

In the first control experiment, we fabricated PDA micelles using the commercially available tricosa-10,12-diynoic acid and polymerized them by 254 nm irradiation. Because of the absence of azo chromophores, these micelles do not possess the H- or J-like aggregations and their stabilization properties. The PDA micelles without azo chromophores show *irreversible* thermochromism after heating to 90 °C.

In the second control experiment, we studied the thermochromism of polyAzoDA micelles in the mixture of DMSO/water. As mentioned above, the aggregation in the polyAzoDA micelles can be gradually destroyed when the concentration of DMSO is increased. We expect that when the aggregation is

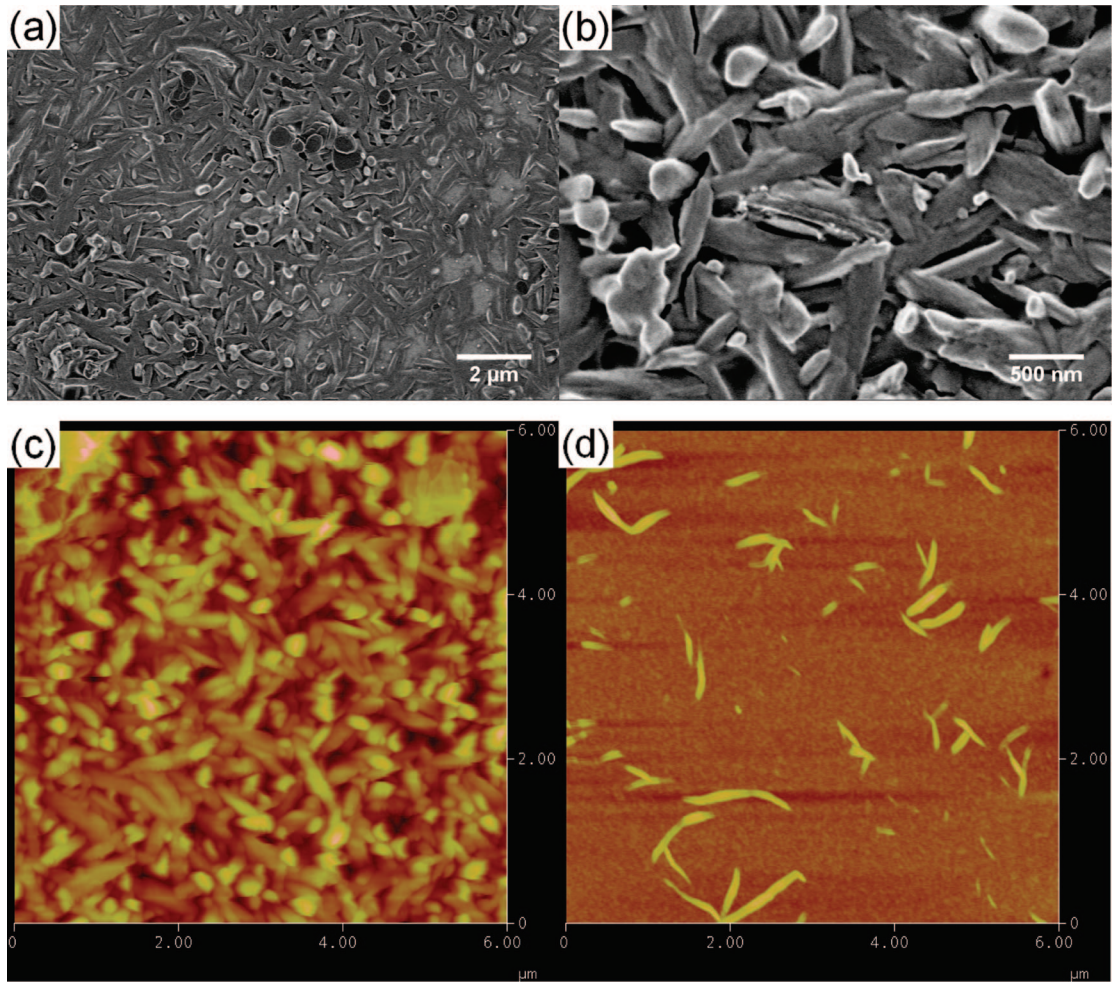

Figure 4. Morphology of polyAzoDA micelles: (a, b) SEM images at different magnifications; AFM images of a drop-cast sample (c) and a spin-coating sample (d). (c) and (d) are 6 μm × 6 μm images.

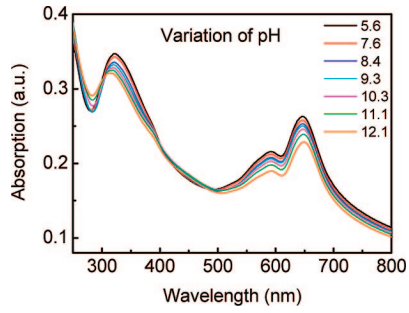

Figure 5. UV−vis absorption spectra of polyAzoDA micelles at different pH recorded at room temperature. The decrease in absorption as pH increases is due to concentration diluting when adjusting the pH.

destroyed, the thermochromism of polyAzoDA micelles will become irreversible. As shown in the Supporting Information, the thermochromism of polyAzoDA micelles is still reversible using DMSO concentrations of 16.7%, 33.3%, and 50%. If we increase the concentration of DMSO to 66.7%, the thermochromism becomes partly reversible, as we observe that the blue micelles change to a slightly different red color after heating, and after cooling the micelles change to purple but not to blue. If the concentration of DMSO is further increased to 83.3%, the blue micelles change to the different red color after heating. But the micelles keep red after cooling. These observations demonstrate that the thermochromism of polyAzoDA micelles

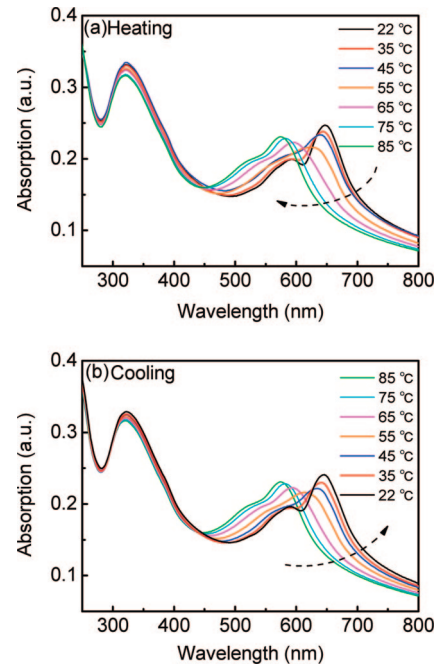

Figure 6. UV−vis absorption spectra of polyAzoDA micelles (a) during heating and (b) during cooling.

becomes irreversible if the additional stabilization by the aggregation of the azo chromophores is missing.

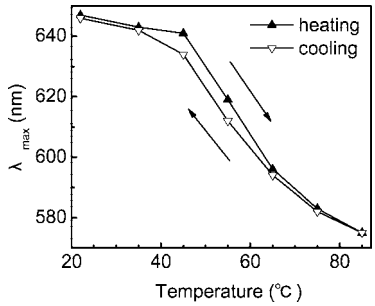

Figure 7. Wavelengths of the absorption peaks of polyAzoDA as a function of temperature during the heating and cooling processes.

Actually, the successful colorimetric reversibilities of PDA reported so far are based on the other enhancement factors, such as the enhanced hydrogen bonding,[14−20] both hydrogen-bonding and strong aromatic interactions,[14,15,21] ionic interactions,[22] or covalent modification[23,24] among the substituent groups of PDAs. In contrast, the reversible thermochromism of polyAzoDA micelles presented here is caused by the improved micelle stability, which is induced by the aggregation of the azo chromophores.

When the pH of polyAzoDA micelles is changed from 5.6 to 9.6, the thermochromism of polyAzoDA micelles also remains fully reversible as indicated by the fully reversible color changes. This means the reversible thermochromism of polyAzoDA micelles exists in a broad pH range which was not achieved before to the best of our knowledge.

Conclusion

In summary, a novel azo chromophore functionalized diacetylene molecule was designed and synthesized. This novel molecule is used to prepare self-assembled cylindrical micelles. The micelles were polymerized under the irradiation of 254 nm light. The azobenzene groups formed aggregates in the cylindrical micelles. The aggregation of azobenzene groups induced sufficient stability of the micelles and enabled reversible thermochromism of PDA at temperatures up to 90 °C in a broad pH range. Compared with other methods, aggregation provides a new way for designing PDAs with reversible color changes. The advantage of aggregation is that it can improve the pH stability of the PDA and aggregation can be easily achieved in films, micelles, or vesicles. To the best of our knowledge, we are not aware of any other demonstration of pH stable PDAs with fully reversible thermochromism. The stability to pH and reversible thermochromism of polyAzoDA also provides platforms for specific sensing, molecular switches, and other applications. The special cylindrical micelle structure is interesting to fabricate new anisotropic nanomaterials.

Acknowledgment. This work is partly supported by NSFC (No. 50573071, No. 50533040, No. 50703038, No. 50773075, and No. 50640420265), National Basic Research Program of China (No. 2006cb302900), and Chinese Academy of Sciences (No. kjcx2.yw.H02). S. Wu gratefully acknowledges financial support from the joint doctoral promotion program of the Chinese Academy of Sciences and the Max Planck Society. The authors thank G. Glasser, M. Jahja, and Dr. Z. Cheng (MPI-P) for their help.

Supporting Information Available: Synthesis, ^{1}H NMR spectra, FTIR spectrum, mass spectrum, UV−vis absorption spectra, and color pictures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lu, Y.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. *Nature (London)* **2001**, *410*, 913–197.
(2) Charych, D. H.; Nagy, J. O.; Spevak, W.; Bednarski, M. D. *Science* **1993**, *261*, 585–588.
(3) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.
(4) Schott, M. *J. Phys. Chem. B* **2006**, *110*, 15864–15868.
(5) Chae, S. K.; Park, H.; Yoon, J.; Lee, C. H.; Ahn, D. J.; Kim, J.-M. *Adv. Mater.* **2007**, *19*, 521–524.
(6) (a) Tamura, H.; Mino, N.; Ogawa, K. *Thin Solid Films* **1989**, *179*, 33–39. (b) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1992**, *8*, 594–598. (c) Cheng, Q.; Stevens, R. C. *Langmuir* **1998**, *14*, 1974–1976. (d) Cheng, Q.; Yamamoto, M.; Stevens, R. C. *Langmuir* **2000**, *16*, 5333–5342. (e) Song, J.; Cheng, Q.; Kopta, S.; Stevens, R. C. *J. Am. Chem. Soc.* **2001**, *123*, 3205–3213. (f) Kew, S. J.; Hall, E. A. H. *Anal. Chem.* **2006**, *78*, 2231–2238.
(7) Tashiro, K.; Nishimura, H.; Kobayashi, M. *Macromolecules* **1996**, *29*, 8188–8196.
(8) Kolusheva, S.; Shahal, T.; Jelinek, R. *J. Am. Chem. Soc.* **2000**, *122*, 776–780.
(9) Yoon, J.; Chae, S. K.; Kim, J.-M. *J. Am. Chem. Soc.* **2007**, *129*, 3038–3039.
(10) Gill, I.; Ballesteros, A. *Angew. Chem.* **2003**, *115*, 3386–3389.
(11) Kim, J. -M.; Lee, Y. B.; Yang, D. H.; Lee, J. S.; Lee, G. S.; Ahn, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 17580–17581.
(12) Lee, J.; Kim, H.-J.; Kim, J. *J. Am. Chem. Soc.* **2008**, *130*, 5010–5011.
(13) Ma, G.; Müller, A. M.; Bardeen, C. J.; Cheng, Q. *Adv. Mater.* **2006**, *18*, 55–60.
(14) Ahn, D. J.; Chae, E.-H.; Lee, G. S.; Shim, H.-Y.; Chang, T.-E.; Ahn, K.-D.; Kim, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 8976–8977.
(15) Kim, J.-M.; Lee, J.-S.; Choi, H.; Sohn, D.; Ahn, D. J. *Macromolecules* **2005**, *38*, 9366–9376.
(16) Lee, S.; Kim, J.-M. *Macromolecules* **2007**, *40*, 9201–9204.
(17) Park, H.; Lee, J.-S.; Choi, H.; Anh, D. J.; Kim, J.-M. *Adv. Funct. Mater.* **2007**, *17*, 3447–3455.
(18) Jonas, U.; Shah, K.; Norvez, S.; Charych, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 4580–4588.
(19) Yuan, Z.; Lee, C.-W.; Lee, S.-H. *Angew. Chem., Int. Ed.* **2004**, *43*, 4197–4200.
(20) Gu, Y.; Cao, W.; Zhu, L.; Chen, D.; Jiang, M. *Macromolecules* **2008**, *41*, 2299–2303.
(21) Hammond, P. T.; Rubner, M. F. *Macromolecules* **1997**, *30*, 5773–5782.
(22) Huang, X.; Jiang, S.; Liu, M. *J. Phys. Chem. B* **2005**, *109*, 114–119.
(23) Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J. Am. Chem. Soc.* **2005**, *127*, 12782–12783.
(24) Peng, H.; Tang, J.; Yang, L.; Pang, J.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J. Am. Chem. Soc.* **2006**, *128*, 5304–5305.
(25) (a) Steed, J. W.; Atwood, J. L. In *Supramolecular Chemistry*; John Wiley & Sons: New York, 2000; Chapter 1. (b) Philpott, M. R.; Lee, J. W. *J. Chem. Phys.* **1972**, *57*, 2026–2033. (c) Möbius, D. *Adv. Mater.* **1995**, *7*, 437–443.
(26) (a) Kasha, M. *Spectroscopy of the Exited State*; Plenum: New York, 1976; pp 337−363. (b) McRae, D. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721–722.
(27) (a) Menzel, H.; Weichart, B.; Schmidt, A.; Paul, S.; Knoll, W.; Stumpe, J.; Fischer, T. *Langmuir* **1994**, *10*, 1926–1933. (b) Stumpe, J.; Fischer, T.; Menzel, H. *Macromolecules* **1996**, *29*, 2831–2842.
(28) Han, M.; Ichimura, K. *Macromolecules* **2001**, *34*, 90–98.
(29) Tong, X.; Cui, L.; Zhao, Y. *Macromolecules* **2004**, *37*, 3101–3112.
(30) Zakrevskyy, Y.; Stumpe, J.; Faul, C. F. J. *Adv. Mater.* **2006**, *18*, 2133–2136.
(31) Tejedor, R. M.; Oriol, L.; Serrano, J. L.; Ureña, F. P.; González, J. J. L. *Adv. Funct. Mater.* **2007**, *17*, 3486–3492.
(32) Kuiper, J. M.; Engberts, J. B. F. N. *Langmuir* **2004**, *20*, 1152–1160.
(33) Deng, Y.; Li, Y.; Wang, X. *Macromolecules* **2006**, *39*, 6590–6598.
(34) Bo, Q.; Zhao, Y. *Langmuir* **2007**, *23*, 5746–5751.
(35) (a) Su, W.; Luo, Y.; Yan, Q.; Wu, S.; Han, K.; Zhang, Q.; Gu, Y.; Li, Y. *Macromol. Rapid Commun.* **2007**, *28*, 1251–1256. (b) Su, W.; Han, K.; Luo, Y.; Wang, Z.; Li, Y.; Zhang, Q. *Macromol. Chem. Phys.* **2007**, *208*, 955–963.
(36) Kunitake, T. *Angew. Chem., Int. Ed.* **1992**, *31*, 709–726.
(37) Ma, A.; Jen, K. Y.; Dalton, L. R. *Adv. Mater.* **2002**, *14*, 1339–1365.
(38) (a) Zimmerman, G.; Chow, L.; Paik, U. *J. Am. Chem. Soc.* **1958**, *80*, 3528–3531. (b) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915–1925.
(39) (a) Anzaj, J. I.; Osa, T. *Tetrahedron* **1994**, *50*, 4039–4070. (b) Whitten, D. G.; Chen, L. H.; Geiger, H. C.; Perlstein, J.; Song, X. S. *J. Phys. Chem. B* **1998**, *102*, 10098–10111. (c) Kinoshita, T. *J. Photochem. Photobiol., B* **1998**, *42*, 12–19. (d) Pedrosa, J. M.; Romero, M. T. M.; Camacho, L.; Mobius, D. *J. Phys. Chem. B* **2002**, *206*, 2583–2591.
(40) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35–48.

(41) Tieke, B.; Graf, H.-J.; Wegner, G.; Naegele, B.; Ringsdorf, H.; Banerjie, A.; Day, D.; Lando, J. B. *Colloid Polym. Sci.* **1977**, *255*, 521–531.
(42) Koch, H.; Ringsdorf, H. *Macromol. Chem. Phys.* **1981**, *182*, 255–259.
(43) Tieke, B.; Wegner, G.; Naegele, D.; Ringsdorf, H. *Angew. Chem., Int. Ed.* **1976**, *15*, 764–765.
(44) Lieser, G.; Tieke, B.; Wegner, G. *Thin Solid Films* **1980**, *68*, 77–90.
(45) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed.* **1988**, *27*, 113–158.
(46) Israelachvili, J. N. In *Intermolecular and Surface Forces*; Academic: San Diego, 1985; Chapter 16.
(47) Soo, P. L.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 923–938.

MA801709N