Polymer Colloids

International Edition: DOI: 10.1002/anie.201604294
German Edition: DOI: 10.1002/ange.201604294

Stimuli-Responsive Shape Switching of Polymer Colloids by Temperature-Sensitive Absorption of Solvent

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***Abstract:** The dynamic manipulation of colloidal particle shape offers a novel design mechanism for the creation of advanced responsive materials. To this end, we introduce a versatile new strategy for shape control of anisotropic polymeric colloidal particles. The concept utilizes temperature-sensitive absorption of a suitable solvent from a binary mixture. Specifically, increasing the temperature in the vicinity of the demixing transition of a binary mixture causes more solvent to be absorbed into the polymeric colloidal particle, which, in turn, lowers the glass transition temperature of the polymer inside the particle, with a concomitant decrease in viscosity. The balance between the internal viscosity and surface tension of the particle is thus disrupted, and the anisotropic shape of the particle shifts to become more spherical. Subsequent rapid temperature quenching can halt the process, leaving the particle with an intermediate anisotropy. The resultant shape anisotropy control provides new routes for studies of the phase transitions of anisotropic colloids and enables the fabrication of unique particles for materials applications.*

The ability to precisely engineer colloidal particle properties is important for the fundamental exploration of self-assembly and for applications in drug delivery and medical diagnostics.[1] Particle shape anisotropy is a particularly useful physical property because it can significantly affect complex fluid rheology, particle packing, phase behavior and responsiveness to external fields,[1b,2] capillary interactions,[3] and Brownian dynamics.[4] However, in contrast to properties such as particle size and surface chemistry, which can be easily tuned by external stimuli,[5] comparatively few stimuli-responsive control schemes for colloidal particle shape have been developed.[6]

Herein, we introduce a simple strategy to induce anisotropic colloidal particles to change shape in a stimuli-responsive manner. The new strategy demonstrates a broadly applicable scheme that employs the absorption of one fluid from a binary mixture to modify the glass transition and viscosity of the polymer-containing colloidal particle. The method, which differs from previous work that relies on a specific polymer with low glass-transition temperature,[6a] can be applied to common polymeric particles. Our demonstration employs anisotropic polystyrene (PS) particles dispersed in a water/2,6-lutidine (WL) mixture, where the binary fluid component 2,6-lutidine is preferentially absorbed by the particles (Figure 1). Furthermore, the absorption of 2,6-lutidine can be easily tuned by a small change in temperature. An increase in temperature toward the WL demixing transition temperature, T_p, enhances the absorption of 2,6-lutidine into the particles and ,in turn, lowers the glass transition temperature of the polymer (the solubility parameter for polystyrene is 21.1 $(\mathrm{MPa})^{0.5}$, whereas that for 2,6-lutidine is 21.9 $(\mathrm{MPa})^{0.5}$).[7] As a result, the particle is effectively softened. When the particle is softened, the particle surface tension dominates the shape of the particle, "turning on" the anisotropy of the particle and shifting its shape towards that of a sphere.[6a] Subsequent rapid temperature quenching can halt the process, leaving the particle with an intermediate anisotropy. In this way, the balance between viscosity and the surface tension of the colloidal particle is readily controlled by the temperature of the binary mixture,

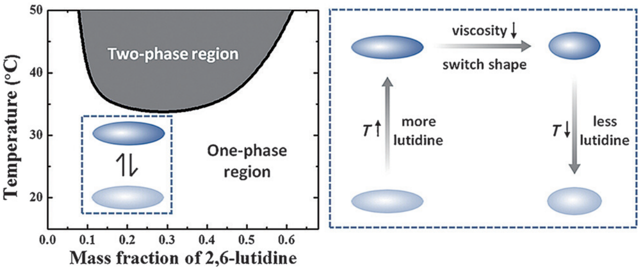

Figure 1. Left: The shape switching of ellipsoidal particles in the context of the phase diagram of binary water/2,6-lutidine mixtures. The thick solid line indicates the coexistence curve of the mixtures.[8] The dashed rectangle highlights the region in which and the process whereby reversible, temperature-dependent absorption of 2,6-lutidine by the colloidal particle occurs. The amount of absorbed solvent increases (more blue shading) as the temperature is raised close to the phase boundary. Right: The associated ellipsoidal particle shape switching, with a mass fraction of 2,6-lutidine of $C_L = 0.2$, as in the other figures. Briefly, the increase of temperature is accompanied by enhancement of 2,6-lutidine absorption, which causes a decrease in the viscosity of the polymer within the particle, and thus activates the shape switching from ellipsoid to sphere due to a competition between surface tension and viscosity. A rapid decrease of temperature leads to recovery of the particle internal viscosity and stops the shape transformation.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201604294.

which, in turn, leads to the dynamic switching of the shape of the anisotropic particle.

The experiments employed micrometer-sized polystyrene (PS) ellipsoids [9] suspended in the WL mixture, with the 2,6-lutidine mass fraction (C_L) set to 0.2. At room temperature (20 °C), that is, far below the glass transition temperature of PS ($T_g \approx 105$ °C), the ellipsoids maintain their shapes without change because the viscosity of the polymer is very high (Figure 2 a). Increasing the temperature enhances the absorption of 2,6-lutidine, a good solvent for PS, and the T_g of the polymer within the PS particle is lowered to 30 °C. This temperature-sensitive absorption is confirmed by laser scanning confocal microscopy and UV spectroscopy measurement[10] (see Figures S1–S4 in the Supporting Information), and the change of the T_g due to the absorption is clarified by differential scanning calorimetry (see Figures S5, S6 in the Supporting Information). Therefore, the viscosity of the particle decreases dramatically at 33 °C (still below the T_p of the WL mixture), and the surface tension begins to drive the shape switching of the particle: the non-spherical shape relaxes continuously to the energetically favorable spherical shape (Figure 2 c; Supporting Information, Movie S2 in the Supporting Information). Importantly, the shape switching can be stopped at any time by rapidly cooling the system to 20 °C. Thus, an intermediate ellipsoidal shape can be preserved (Figure 2 b; Supporting Information, Movie S1).

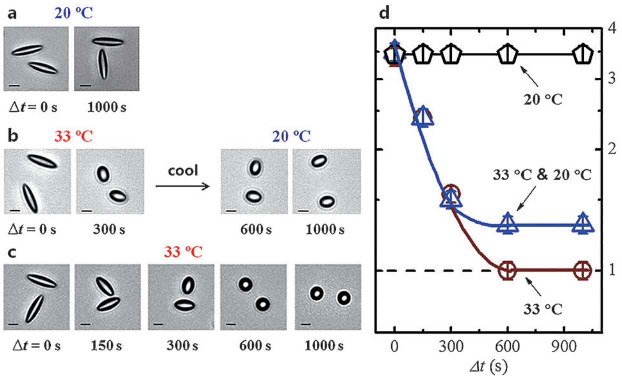

Figure 2. Bright-field micrographs of the stimuli-responsive shape transformation of PS ellipsoids in a water/2,6-lutidine mixture ($C_L = 0.2$). a) At 20 °C, PS ellipsoids maintain their shape. b) Heating the system to 33 °C activates the shape-switching of the PS ellipsoids; cooling the system stops the transformation, and the new shape is preserved. c) Without cooling, particles transform continuously from ellipsoids to spheres. d) The corresponding aspect ratios (*AR* = long axis/short axis) of the particles are shown in a, b, and c. Scale bar: 2 μm. See the Supporting Information Movies S1 and S2 for the videos of the shape transformations in (b) and (c).

We reproduced this shape switching behavior with other anisotropic polystyrene particles, such as barrels and discs (Figure 3, and Movies S3, S4 in the Supporting Information). Moreover, we have applied the strategy to colloidal particles composed of other solubility-matched polymers such as polymethyl methacrylate (PMMA); the stimuli-responsive shape switching of these particles is consistent with that of PS particles (Figure S7 in the Supporting Information).

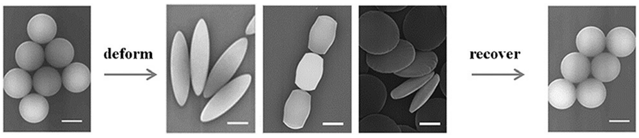

Figure 3. Scanning electron microscope (SEM) images of the shape-switching particles. Left: The initial PS spheres; Middle: Non-spherical PS particles: ellipsoids, barrels, and discs made by mechanical stretching and compression; Right: PS spheres after shape recovery in a WL mixture ($C_L = 0.2$). Scale bar: 2 μm.

Next, we show how shape anisotropy control can be utilized to drive new soft matter phenomena in situ. As a first example, we consider a disordered, two-dimensional assembly of PS ellipsoids in the WL mixture (Figure 4). Shape anisotropy variation enables us to probe new trajectories in the phase diagram. Initially, the ellipsoids have a relatively small anisotropy (aspect ratio, $AR \approx 4.3$), so we do not expect ellipsoids to form a uniform nematic phase, and indeed disordered structures with nematic domains are observed (Figure 4 a). By modulating the temperature, we systematically vary the aspect ratio of the ellipsoids from 4.3 to 1.4 to 1.0 (Figure 4 a–c). These variations in shape anisotropy induce a phase transition from a disordered (glass) packing to an ordered (crystalline) packing. Such a transition is reflected by the corresponding radial distribution functions, $g(r)$ (Figure 4 e). The amplitude and the number of the oscillations of $g(r)$ increase as the ellipsoid aspect ratio decreases to unity, that is, as the anisotropic ellipsoidal particles transform to isotropic spheres. We envision that such particles, with continuously tunable shape anisotropy, will offer an exciting new model system for the study of phase transition mecha-

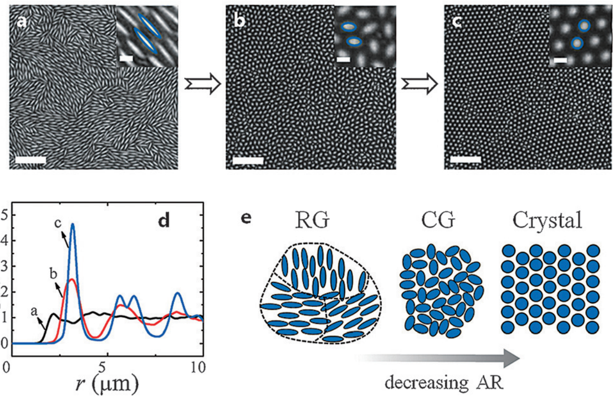

Figure 4. Shape transformations of an assembly of PS ellipsoids by a temperature trigger in a WL mixture ($C_L = 0.2$). a)–c) Bright-field micrographs. From (a) to (c), the ellipsoid aspect ratio *AR* is 4.4, 1.4, 1.0, respectively, with corresponding area fractions $\phi = 0.714$, 0.693, and 0.725, respectively. Insets: enlarged micrographs with blue curves to highlight the particle shape. d) Radial distribution function g(r) for panels a–c. e) Illustration of phases of the ellipsoid assemblies in two dimensions. As the aspect ratio decreases, the ellipsoids form a rotational glass (RG) with nematic domains, a conventional glass (CG) without nematic domains, and finally a crystal when $AR \approx 1$. For panels (a)—(c), the scale bars are 20 μm (main figure) and 2 μm (inset).

nisms, glass dynamics of ellipsoid systems,[11] and jamming via shape control rather than packing volume fraction control.

Besides probing phase transitions and self-assembly processes, the novel shape manipulation strategy enables fabrication of highly unusual colloidal particles via surface tension modulation. For example, when a thin layer of gold is coated onto one side of the non-spherical PS particles, the magnitude and direction of the particle deformation can be controlled and manipulated to produce particles with remarkable shapes (Figure 5). For ellipsoids, the thin gold coating on the curved particle surface impedes the return of the particles to the spherical shape and transforms them into ox-horn-like shapes (Figure 5a,b). For discs, due to stress-driven instabilities on the flat surface,[12] the gold side of the particles becomes wrinkled, resulting in Janus particles with both chemical (gold) and physical (wrinkle) anisotropies (Figure 5c,d). We expect these novel anisotropic particles to exhibit heretofore unexplored self-assembly behavior[13] and to offer potential applications in biomaterials, for example, if the gold is further modified via thiol chemistry.[1b,e] In summary, a facile strategy for the dynamic control of the shape anisotropy of polymer-based colloidal particles has been proposed and demonstrated. The strategy utilizes thermosensitive absorption of a suitable solvent from a binary fluid mixture to adjust the balance between the internal viscosity and surface tension of the particle and thereby stimulate shape changes. This shaping strategy is general and can be applied to various polymers. We have demonstrated the fabrication of novel colloidal particles with special anisotropic properties that could permit the design of new materials. Moreover, we have taken first steps to show how the in situ control of the shape of the colloidal particles provides a novel pathway to investigate shape effect mechanisms in phase behavior, such as those that arise in glasses, jammed systems, and crystals.

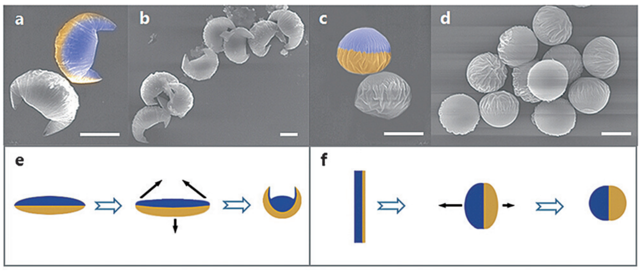

Figure 5. Fabrication of colloidal particles with novel shapes in a WL mixture ($C_L = 0.2$). Top panel: SEM images of the special PS colloidal particles: ox-horn-like (a, b) and Janus corrugated particles (c, d). Scale bar: 2 μm. Bottom panel: Particle fabrication. A thin layer of gold is coated onto one side of particle (yellow shading); then, during the shape recovery period, the different balances between the surface tension, elasticity of the metal coating, and viscosity of the particle interior produce uniquely shaped particles. The solid black arrows indicate the force directions, and the lengths of the arrows indicate the force magnitudes.

Acknowledgements

Z.Z. acknowledges financial support of the National Basic Research Program of China (No. 2012CB821500), the National Natural Science Foundation of China (Nos. 21174101, 21522404, 11574222), and the Project for Jiangsu Scientific and Technological Innovation Team (2013). H.W. acknowledges financial support from Jiangsu Planned Projects for Postdoctoral Research Funds. A.G.Y. acknowledges support from NSF Grant DMR12-05463, the PENN MRSEC DMR11-20901, and NASA NNX08AO0G.

Keywords: absorption · colloids · polymers · shape-switching · temperature sensitivity

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9952–9955
Angew. Chem. **2016**, *128*, 10106–10109

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[1] a) M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101–113; b) S. Mitragotri, J. Lahann, *Nat. Mater.* **2009**, *8*, 15–23; c) R. Langer, D. A. Tirrell, *Nature* **2004**, *428*, 487–492; d) D. S. Kohane, *Biotechnol. Bioeng.* **2007**, *96*, 203–209; e) S. Sacanna, D. J. Pine, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 96–105; f) B. Li, M. Wang, Z. Cheng, G. Chen, Z. Zhang, *Macromol. Rapid Commun.* **2015**, *36*, 1200–1204.

[2] a) B. Madivala, J. Fransaer, J. Vermant, *Langmuir* **2009**, *25*, 2718–2728; b) F. M. van der Kooij, E. S. Boek, A. P. Philipse, *J. Colloid Interface Sci.* **2001**, *235*, 344–349; c) A. Donev, I. Cisse, D. Sachs, E. Variano, F. H. Stillinger, R. Connelly, S. Torquato, P. M. Chaikin, *Science* **2004**, *303*, 990–993.

[3] a) J. C. Loudet, A. M. Alsayed, J. Zhang, A. G. Yodh, *Phys. Rev. Lett.* **2005**, *94*, 018301; b) P. J. Yunker, T. Still, M. A. Lohr, A. G. Yodh, *Nature* **2011**, *476*, 308–311.

[4] Y. Han, A. M. Alsayed, M. Nobili, J. Zhang, T. C. Lubensky, A. G. Yodh, *Science* **2006**, *314*, 626–630.

[5] a) G. Romeo, A. Fernandez-Nieves, H. M. Wyss, D. Acierno, D. A. Weitz, *Adv. Mater.* **2010**, *22*, 3441–3445; b) S. R. Sershen, S. L. Westcott, N. J. Halas, J. L. West, *J. Biomed. Mater. Res.* **2000**, *51*, 293–298; c) J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, R. Langer, *Science* **2003**, *299*, 371–374.

[6] a) J. W. Yoo, S. Mitragotri, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 11205–11210; b) M. P. Chien, A. M. Rush, M. P. Thompson, N. C. Gianneschi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5076–5080; *Angew. Chem.* **2010**, *122*, 5202–5206; c) J. W. Yoo, N. Doshi, S. Mitragotri, *Adv. Drug Delivery Rev.* **2011**, *63*, 1247–1256.

[7] a) C. L. Yaws, *Thermophysical Properties of Chemicals and Hydrocarbons, 1st ed.*, William Andrew, Norwich, **2008**; b) L. H. Sperling, Introduction to Physical Polymer Science 4th ed.;Wiley Inter-Science: Hoboken, NJ, **2006**; c) W. G. Bi, X. Y. Wu, E. K. L. Yeow, *Langmuir* **2012**, *28*, 11056–11063.

[8] C. A. Grattoni, R. A. Dawe, C. Y. Seah, J. D. Gray, *J. Chem. Eng. Data* **1993**, *38*, 516–519.

[9] a) C. C. Ho, A. Keller, J. A. Odell, R. H. Ottewill, *Colloid Polym. Sci.* **1993**, *271*, 469–479; b) J. A. Champion, Y. K. Katare, S. Mitragotri, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 11901–11904.

[10] a) J. H. Lee, I. J. Gomez, V. B. Sitterle, J. C. Meredith, *J. Colloid Interface Sci.* **2011**, *363*, 136–144; b) M. Bradley, N. Bruno, B. Vincent, *Langmuir* **2005**, *21*, 2750–2753; c) K. Hirayama, *Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds, 1st ed.*, Plenum, New York, **1967**.

[11] a) Z. Zheng, F. Wang, Y. Han, *Phys. Rev. Lett.* **2011**, *107*, 065702; b) Z. Zheng, R. Ni, F. Wang, M. Dijkstra, Y. Wang, Y. Han, *Nat. Commun.* **2014**, *5*, 3829.

[12] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, G. M. Whitesides, *Nature* **1998**, *393*, 146 – 149.

[13] a) C. Yu, J. Zhang, S. Granick, *Angew. Chem. Int. Ed.* **2014**, *53*, 4364 – 4367; *Angew. Chem.* **2014**, *126*, 4453 – 4456; b) A. A. Shah, B. Schultz, W. Zhang, S. C. Glotzer, M. J. Solomon, *Nat. Mater.* **2015**, *14*, 117 – 124.

Received: May 3, 2016
Revised: June 9, 2016