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Photoinduced reversible transmittance modulation of rod–coil type diblock copolymers containing azobenzene in the main chain†

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Photoinduced reversible transmittance modulation was achieved with the self-assembled block copolymer micelles. A large conformational change of the well-defined rod–coil diblock copolymers containing azobenzene and ether groups in the main chain of the rod block induced a remarkable macroscopic change which can be observed with the naked eye.

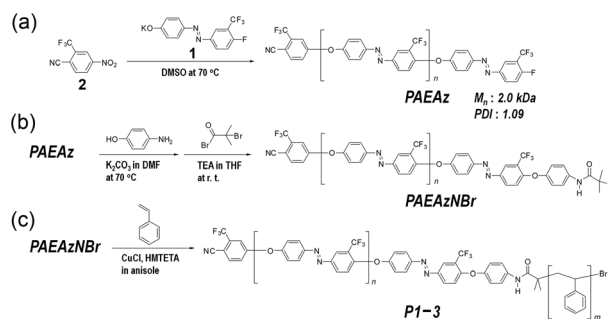
Nanostructured materials responsive to external stimuli such as temperature,^{1a} pH,^{1b} chemicals,^{1c} and light^{1d} have attracted considerable research interest due to their potential application in many areas including integrated optical devices^{2a} and biomedical drug delivery.^{2b} Among many stimuli, light has distinctive advantages such as controllable selectivity of illumination areas and periods, remote incidents, and so forth. Photoresponsive polymeric materials which perceive and shut off the light of undesired wavelengths have tremendous potential for intelligent optical devices.³ However, the development of nanostructured polymeric materials to adjust light transmittance based on the amount of external irradiation is still a great challenge. Recently, photo-responsive morphological changes of micellar aggregates in solutions by UV and visible light were achieved by incorporating azobenzene into polymeric materials.⁴ The photoresponsive changes were mainly attributed to the dipole moment changes of molecules induced by photoisomerization of azobenzene groups together with hydrophilic–hydrophobic balance shifts which destabilize the self-assembled aggregates.

Self-assembled nanostructures of block copolymers both in thin films⁵ and in solutions⁶ have been intensively studied in perspective of development of nanostructured organic materials, and construction of complex nanostructured materials by self-assembly usually requires precisely defined nanomolecules where the molecular structures become primary factors to determine morphologies of self-assembled nanostructures.⁷ Among many different types of diblock copolymers, self-assembly behavior of diblock copolymers consisting of a rigid rod and a flexible coil is interesting because of the conformational asymmetry between each block and various functionalities on main chains of rod segments.⁸

However, preparation of well-defined condensation polymers has been very difficult until the development of chain-growth condensation polymerization (CGCP),⁹ while controlled radical polymerizations of diverse vinyl monomers have been well established.¹⁰ Simple combination of CGCP and atom transfer radical polymerization (ATRP) allows straightforward synthesis of rod–coil type diblock copolymers composed of condensation and addition blocks with controlled molecular weights and molecular weight distributions.¹¹

Here we report the reversible dramatic transmittance changes resulting from photoinduced aggregation and segregation of self-assembled block copolymer micelles composed of well-defined rod–coil type diblock copolymers. The block copolymers were synthesized through CGCP for rod segments containing azobenzene units in the main chain, and subsequent ATRP of styrene with a proper macroinitiator for coil blocks. A nucleophilic aromatic substitution (S_NAr) reaction was a key for synthesis of well-controlled poly(arylene ether azobenzene) (PAEAz) by displacement of the leaving group (*i.e.* F or NO₂) activated by a trifluoromethyl group.¹² In cyclohexane, uniform micellar aggregates of the diblock copolymer were formed as the spherical structure consisted of the core rod and the periphery coil. Irradiated by UV light, the transmittance of the homogenous solution decreased down to maximum *ca.* 22%, and became turbid, but returned to a clear solution when exposed to visible light. The solution obstructs incident light whenever a certain amount of UV irradiation is illuminated.

Well-defined rod–coil type diblock copolymers (**P1–3**) prepared in this study are shown in Scheme 1, and their physical properties are summarized in Table 1. Details of the synthetic methods and



Scheme 1 (a) Synthesis of PAEAz through CGCP. (b) End-group modification of PAEAz. (c) ATRP of styrene with the macroinitiator for synthesizing well-defined block copolymers.

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Table 1 Characterization of the block copolymers

Samples	M_n [GPC] ^a	M_n [NMR] ^b	M_w/M_n ^a	T_g ^c /°C	T_{d5} ^d /°C
P1	11 300	12 700	1.18	104.2	354
P2	15 500	16 100	1.24	104.4	347
P3	28 900	25 200	1.25	108.0	362

^a Estimated by THF-GPC based on PS standards. ^b Calculated by ¹H NMR spectra of diblock copolymers in CDCl₃. ^c Measured by DSC at the second scan with a heating rate of 5 °C min⁻¹ under nitrogen flow. ^d 5% weight loss temperature measured by TGA with a heating rate of 10 °C min⁻¹ under nitrogen flow.

characterization of the block copolymers are described in the ESI.† Polycondensation of the AB' type monomer (**1**) proceeded in a chain-growth manner under the certain reaction conditions (ESI†). CGCP of **1** produced well-defined PAEAz (M_n : 2.0 kDa, PDI: 1.09) with the proper feed ratio. The molecular weights of the polymers were well matched with the theoretical values as the conversion of the monomers increased, and the constant number of propagating species was maintained. However, it was difficult to obtain high molecular weights (>5 kDa) of polymers with a narrow polydisperse index (PDI) presumably because of the transesterification caused by the strongly activated ether bond between an initiator moiety and a monomer. For ATRP of coil blocks, the end groups of the polymers were modified to macroinitiator, PAEAzNBr, and used for polymerization of styrene monomers. GPC analysis of the polymerization product revealed that all the macroinitiators were not initiated, indicating that the efficiency of the amide-linked macroinitiator was rather low in ATRP of styrene.¹³ However, the unreacted macroinitiator was easily separated from the block copolymer by extraction with cyclohexane (ESI†).

The synthesized PAEAz is soluble in many organic solvents including NMP, THF, ethylacetate, toluene, and chloroform, but is not soluble in cyclohexane that dissolves polystyrene. Therefore, block copolymer micelles of the rod-coil diblock copolymers were prepared by addition of cyclohexane into the THF solution of the diblock copolymers and subsequent dialysis to remove THF. Because the block copolymers (e.g. P3) having molecular weight above 20 kDa were not dissolved in cyclohexane, only the diblock copolymer micelles of P1 and P2 were prepared. A dynamic light scattering (DLS) study (Fig. 1a) of the cyclohexane solutions shows the hydrodynamic diameter of 190 nm of the self-assembled block copolymer micelles with quite narrow distributions (PDI: 0.005), and TEM images (Fig. 1b) reveal the regular spherical shape of the micelles consisting of azo blocks in the core and PS blocks in the shell. The SEM image (Fig. 1c) also shows that the diblock copolymer micelles have narrow size distribution with the diameter of about 90 nm which is less than that of the DLS result due to a contraction of the micelles.

The diblock copolymer micelle showed photoresponsive aggregation and segregation behavior that was large enough to be detected with the naked eye, unlike the previously reported⁴ coil type block copolymer micelles. The clear cyclohexane solution of diblock copolymer micelles became turbid when it was exposed to UV light, but returned to a clear solution with exposure to visible light. Fig. 2a shows a photoinduced reversible transmittance modulation of the self-assembled block copolymer

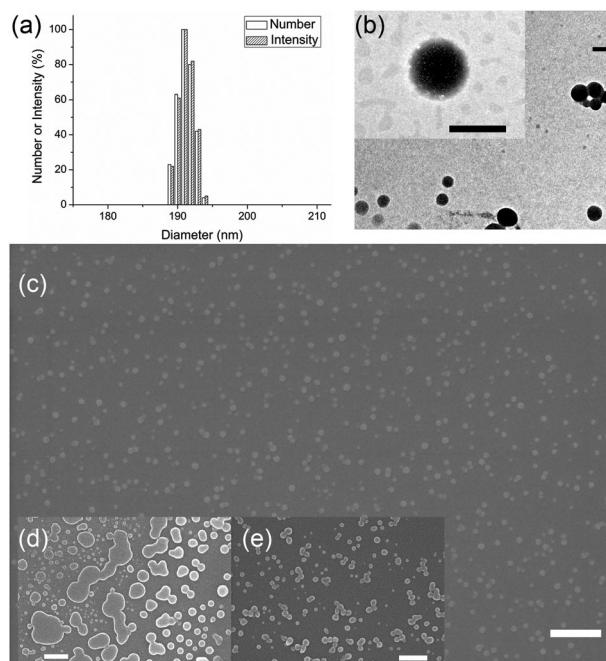


Fig. 1 (a) DLS plots, (b) TEM images on a carbon-coated copper grid, and (c–e) SEM images on a Si wafer of the self-assembled diblock copolymer micelles of P2 prepared in cyclohexane. (a) The blank and patterned columns are the number and intensity MSD values, respectively. (b) With scale bars of 200 nm. The inset is a magnified image. (c) With a scale bar of 800 nm. (d) After UV light irradiation with a scale bar of 900 nm. (e) After UV and subsequent visible light irradiation with a scale bar of 400 nm.

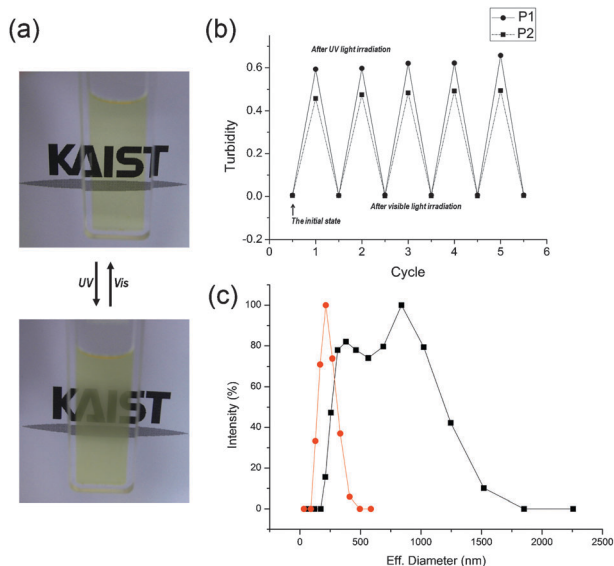


Fig. 2 (a) Photographs, (b) changes in turbidity, and (c) DLS plots of the photoinduced reversible transmittance modulation of the self-assembled diblock copolymer micelles prepared in cyclohexane. (a) (top) The transparent initial or visible-exposed solution; (bottom) the turbid UV-exposed solution of P2, (b) for P1 (circles) and P2 (squares). The turbidity was measured at 700 nm in UV-vis spectra. (c) (squares) The UV-exposed solution; (circles) the subsequent visible-exposed solution.

micelles. The reversible changes in turbidity of the solution were observed with alternating UV and visible light irradiation (Fig. 2b). While the transmittance of the cyclohexane solution

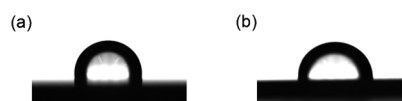


Fig. 3 Photographs of advancing contact angle goniometry for homopolymer **PAEAz** thin films (a) as spin casting (95°). (b) From the UV-exposed solution (82°).

of the **P2** micelle reduced to 30%, the transmittance of the **P1** micelles decreased to 22% because of the larger volume fraction of the azobenzene units in **P1**. The photoinduced transmittance change was the result of the aggregation and segregation of the self-assembled block copolymer micelles with the size change from nanometres to micrometres. The PDI values also increased dramatically from 0.005 to 0.229 (Fig. 1 and 2). Photoisomerization of azobenzene units in the main chains of the rod block directly altered the conformation of the polymer backbone. The changed conformation not only disturbed the self-assembled structures but also induced different geometrical packing parameters.^{4c} And also there is another important change of physical properties as the conformation of azobenzene changed to *cis* from *trans*. It is well known for the azobenzene without substitutions that the elongated *trans* configuration has a zero dipole moment, while the bent *cis* has a dipole moment of ~ 3 D.¹⁴ To check the dipole moment change of the diblock copolymers, the thin films of the polymer were prepared and their contact angles were measured (Fig. 3). The advancing contact angle was greater for the films prepared from the solution without irradiation of UV light than for the films prepared from the solution with UV-exposure. It seems that the increased hydrophilicity of a polar *cis* conformation causes the further aggregation of diblock copolymer micelles in a thermodynamically unstable state in the nonpolar solvent, cyclohexane. Even though the volume fraction of the rod blocks is smaller than that of the coil, the conformational changes of rod blocks are significant and amplified through consecutive conformational changes of the rigid backbone.

To monitor the photoisomerization of azobenzene units of the diblock copolymers, we investigated the UV-visible absorption spectra of the block copolymers (ESI†). As expected, *trans*-to-*cis* isomerization of the azobenzene groups occurred upon irradiation of UV light, and the π - π^* transition absorption bands of the *trans*-azobenzene moieties at around 360 nm decreased with the concomitant increase of the n - π^* transition absorption bands of the *cis* isomer at around 440 nm. After UV light irradiation for several minutes, baseline shifted abruptly because the solution became turbid. However, subsequent irradiation of visible light to the heterogeneous solution restored the original spectrum with stable baseline in a few seconds.

In conclusion, we have demonstrated photoinduced reversible transmittance modulation of the rod-coil diblock copolymer micelle. The well-defined rod-coil type diblock copolymers were synthesized through combination of CGCP and ATRP. The dipole moment change induced by photoisomerization of azobenzene incorporated along the backbone into the rod

segment plays an important role in photoinduced aggregation and segregation of the self-assembled diblock copolymer micelles in cyclohexane. The diblock copolymers containing azobenzene in the main chain are expected to find many interesting applications.

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Notes and references

- (a) Z. Ge, J. Xu, J. Hu, Y. Zhang and S. Liu, *Soft Matter*, 2009, **5**, 3932–3939; (b) M. Krämer, J.-F. Stumbé, H. Türk, S. Krause, A. Komp, L. Delineau, S. Prokhorova, H. Kautz and R. Hagg, *Angew. Chem., Int. Ed.*, 2002, **41**, 4252–4256; (c) J. R. Capadona, K. Shanmuganathan, D. J. Tyler, S. J. Rowan and C. Weder, *Science*, 2008, **319**, 1370–1374; (d) H.-I. Lee, W. Wu, J. K. Oh, L. Mueller, G. Sherwood, L. Peteanu, T. Kowalewski and K. Matyjaszewski, *Angew. Chem., Int. Ed.*, 2007, **46**, 2453–2457.
- (a) J. Hiller, J. D. Mendelsohn and M. F. Rubner, *Nat. Mater.*, 2002, **1**, 59–63; (b) E. Kim, D. Kim, H. Jung, J. Lee, S. Paul, N. Selvapalam, Y. Yang, N. Lim, C. G. Park and K. Kim, *Angew. Chem., Int. Ed.*, 2010, **49**, 4405–4408.
- H. Tsutsui, M. Mikami and R. Akashi, *Adv. Mater.*, 2004, **16**, 1925–1929.
- (a) X. Liu and M. Jiang, *Angew. Chem., Int. Ed.*, 2006, **45**, 3846–3850; (b) G. Wang, X. Tong and Y. Zhao, *Macromolecules*, 2004, **37**, 8911–8917; (c) J.-H. Liu and Y.-H. Chiu, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1142–1148; (d) Y. Zhao, *J. Mater. Chem.*, 2009, **19**, 4887–4895.
- G. Krausch and R. Magerle, *Adv. Mater.*, 2002, **14**, 1579–1583.
- (a) J. Yang, D. Lévy, W. Deng, P. Keller and M.-H. Li, *Chem. Commun.*, 2005, 4345–4347; (b) R. K. O'Reilly, C. J. Hawker and K. L. Wooley, *Chem. Soc. Rev.*, 2006, **35**, 1068–1083; (c) G. Delaittre, C. Dire, J. Rieger and J.-L. Putaux, *Chem. Commun.*, 2009, 2887–2889; (d) T. Higuchi, A. Tajima, K. Motoyoshi, H. Yabu and M. Shimomura, *Angew. Chem., Int. Ed.*, 2009, **48**, 5125–5128; (e) S. J. Holder and N. A. J. M. Sommerdijk, *Polym. Chem.*, 2011, **2**, 1018–1028.
- S. R. Bull, L. C. Palmer, N. J. Fry, M. A. Greenfield, B. W. Messmore, T. J. Meade and S. I. Stupp, *J. Am. Chem. Soc.*, 2008, **130**, 2742–2743.
- (a) S. A. Jenekhe and X. L. Chen, *Science*, 1998, **279**, 1903–1907; (b) H.-D. Koh, J.-W. Park, M. S. Rahman, M. Changez and J.-S. Lee, *Chem. Commun.*, 2009, 4824–4826; (c) D. M. Vriezema, J. Hoogboom, K. Velonia, K. Takazawa, P. C. M. Christianen, J. C. Maan, A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed.*, 2003, **42**, 772–776.
- (a) T. Yokozawa and A. Yokoyama, *Chem. Rev.*, 2009, **109**, 5595–5619; (b) J. Park, M. Seo, H. Choi and S. Y. Kim, *Polym. Chem.*, 2011, **2**, 1174–1179.
- (a) K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990; (b) A. Favier and M.-T. Charreyre, *Macromol. Rapid Commun.*, 2006, **27**, 653–692.
- (a) Y. J. Kim, M. Seo and S. Y. Kim, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1049–1057; (b) J. Park, M. Moon, M. Seo, H. Choi and S. Y. Kim, *Macromolecules*, 2010, **43**, 8304–8313; (c) N. Ajioka, Y. Suzuki, A. Yokoyama and T. Yokozawa, *Macromolecules*, 2007, **40**, 5294–5300.
- (a) I. S. Chung and S. Y. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 11071–11072; (b) Y. J. Kim, I. S. Chung and S. Y. Kim, *Macromolecules*, 2003, **36**, 3809–3811; (c) D. Ka, M. Seo, H. Choi, E. H. Kim and S. Y. Kim, *Chem. Commun.*, 2010, **46**, 5722–5724.
- W. Tang, Y. Kwak, W. Braunecker, N. V. Tsarevsky, M. L. Coote and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2008, **130**, 10702–10713.
- Y. Zhao, in *Smart Light-Responsive Materials, Azobenzene-Containing Polymers and Liquid Crystals*, ed. Y. Zhao and T. Ikeda, John Wiley & Sons, New Jersey, 2009, ch. 6, pp. 215–242.