Polymer Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Nucleobase-grafted supramolecular polymers for tuning the surface properties†

Cite this: *Polym. Chem.*, 2014, **5**, 702

Received 29th August 2013
Accepted 28th October 2013

DOI: 10.1039/c3py01176c

www.rsc.org/polymers

I.-Hong Lin,[a] Chih-Chia Cheng,*[a] Ke-Fong Li,[a] Jem-Kun Chen,[b] Chih-Wei Chiu[b] and Feng-Chih Chang*[c]

Nucleobase-grafted polycaprolactone has been prepared which exhibits amorphous nature, rapid photoresponse and controlled surface properties in the solid state owing to the formation of uracil–diamidopyridine (U–DAP) pairs by induced physical cross-linking. In addition, they can self-organize to alter material behavior with light, switching both optical and thermal properties. Remarkable changes in the surface morphology and the contact angle with water were also observed.

Photochromic materials recently have attracted renewed interest because of their potential technological applications for optical data storage and optical switching.[1] Among photochromic molecules, azobenzene moieties as switching units have been extensively studied for their unique photoisomerization.[2] The azobenzene molecule isomerizes from a stable *trans* state to a metastable *cis* state upon UV irradiation, and the *cis* isomer can be switched back to the *trans* isomer by visible light or heat. The *cis–trans* isomerization of azobenzene is usually accompanied by molecular changes in physical properties such as polarity, viscosity and absorbance. In recent years, several light-induced effects have been reported.[3] For example, Alemani *et al.* observed field-induced *trans–cis* isomerization of 3,3′,5,5′-tetra-*tert*-butylazobenzene, at a height of 5–6 Å from the surface.[4] However, unsubstituted azobenzene has been observed to undergo *trans–cis* isomerization at negative sample bias, with the reverse process occurring at positive bias.[5] When azobenzene is incorporated in a polymer matrix, photoisomerization can generate motions ranging from reorientation of the chromophore to massive motion of the polymer materials.

Supramolecular interactions offer several novel strategies for material design, because noncovalent interactions are inherently reversible, highly tunable, and provide unlimited processablility.[6] These materials utilize noncovalent interactions similar to those found in bio-molecules such as proteins, DNA, and RNA to direct and modulate their 3-D topology.[7] Inspired by natural systems, chemists have explored the use of noncovalent interactions for the construction of supramolecular polymers resulting in responsive materials with properties that can be changed by varying the environmental parameters, such as temperature, pH, redox state or concentration.[8] Several supramolecular structures have been incorporated into polymers to form novel materials with features of conventional polymers while featuring reversibility in the bonding between monomer units.[9] In a previous study, we demonstrated that it is possible to form a RNA-like randomly copolymer by choosing biocomplementary hydrogen bonding recognitions (uracil–adenine; U···A).[10] More recently, we further report the synthesis and assembly behavior of heteronucleobase-functionalized biopolymers.[11] Attachment of multiple hydrogen-bonding units to side chains of polymers results in phase separation and substantial changes in morphology and biocompatibility *in vitro*. Therefore, we expect introduction of a potential route to the combination of noncovalent interactions and photoisomerization in supramolecular polymers. In this study, we prepared a uracil-grafted polycaprolactone (U–PCL) and transformed it into noncovalent network systems through biocomplementary hydrogen bonding recognition in the presence of a diamidopyridine-based azo chromophore (Azo-bisdap, Scheme 1).

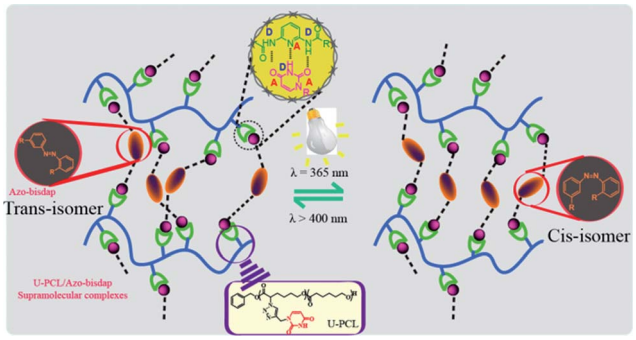
Nucleobase-functional polycaprolactone was synthesized in three steps as shown in Scheme S1 (see the ESI† for full details). In this case, introducing azobenzene-nucleobase cross-linkers into the side-chain polymer could lead to new ways to control large-scale changes in optical and photo-physical properties. The synthesis of the Azo-bisdap involved four steps (Scheme S2†): acryl chloride-terminated azidoundecane was synthesized using an excess of thionyl chloride in the reaction,

[a]*Institute of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan. E-mail: chihchia.ac95g@nctu.edu.tw*

[b]*Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*

[c]*Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan. E-mail: changfc1973@gmail.com*

† Electronic supplementary information (ESI) available: Details of the experiment, NMR spectra, mass spectrometry and ^{1}H NMR spectra of the methylene protons of Azo-bisdap and U-PCL. See DOI: 10.1039/c3py01176c



Scheme 1 Graphical representation of a crosslinked U–PCL/Azo-bisdap complex.

the terminal acryl chloride was end-capped with *N*-(6-aminopyridin-2-yl)acetamide to produce a DAP-terminated azidoundecane, and then the Azo-bisdap was obtained after click chemistry. The copolymer composition was confirmed by the relative ^{1}H NMR spectroscopic absorption peak areas of signals at α-Cl-ε-CL and ε-CL (Table S1†). The properties of the nucleobase-grafted polycaprolactone containing 30% uracil units are the focus of this communication.

Before photochemical studies, we first investigated (Fig. 1) the binding affinity of the intermolecular complex using a ^{1}H NMR titration experiment. The association constants (K_a) for hydrogen-bonded complexes characterized by ^{1}H NMR at 25 °C in chloroform-*d* and the Azo-bisdap concentration systematically increased from 40 to 420 mM. The position of the uracil imide peak in the spectra of the copolymer shifts with increasing concentration of the diamidopyridine host. In addition, the resonances of the amido NHs are relatively broader, indicating a fast exchange rate between the associated and the dissociated uracil–diamidopyridine complex on the NMR time scale.[11] The Bensi–Hildebrand model, a mathematical method of determining the association constant (K_a) from the NMR titration experiment, was employed to fit nonlinear chemical shift data as expected for heteromeric hydrogen bond association with the assumption that the complex was formed in 1 : 1 stoichiometry.[12] A double reciprocal plot based on the association of the Azo-bisdap complex showed a linear relationship as shown in Fig. S4.† The K_a value obtained for copolymer and monomer systems was 23.2 M^{-1}, providing evidence for cooperative binding events on polymer scaffolds.

After conducting these preliminary biocomplementary hydrogen bonding recognition studies, we test the photoisomerization of the U–PCL/Azo-bisdap complex. Upon irradiation with UV light at 365 nm, the absorption band at around 345 nm decreases significantly, while the band at around 435 nm increases slightly as shown in Fig. 2. The absorption bands at 340 and 435 nm are ascribed to π–π* and n–π* transitions, respectively. Spectra overlay suggested the isosbestic point existing around 400 nm. When irradiated with visible light (or in the dark), the π–π* absorption increases with a slight decrease in the n–π* absorption, indicating that the photoisomerization of azobenzene undergoes a change from the *cis* to the *trans* state. The change of the absorption bands induced by UV irradiation is indicative of the photoisomerization of azobenzene from the *trans* to the *cis* state. Similar results were verified in ^{1}H NMR spectroscopy under irradiation with UV light (Fig. S5†): the peak at $\delta = 5.50$ decreases and the peak intensity of the signal at $\delta = 5.46$ increases substantially. The former peak corresponds to the *trans*-isomer and the latter corresponds to the *cis*-isomer. When irradiated with visible light (or in the dark), the results exhibited a reverse trend. This observation indicates that the formation of the supramolecular cross-linked structure is due to photochemical reversibility.

Fig. 3 (a) displays DSC thermograms of both U–PCL and Azo-bisdap, and their blends at various compositions. A single value of the glass transition temperature (T_g) strongly suggests that the U30–PCL/Azo-bisdap blend system is fully miscible with the

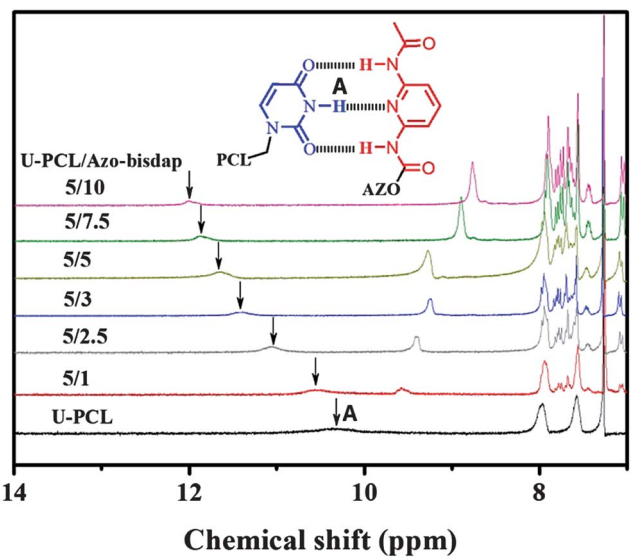


Fig. 1 ^{1}H NMR titration of U–PCL with Azo-bisdap. The chemical shift of the NH group of uracil was monitored.

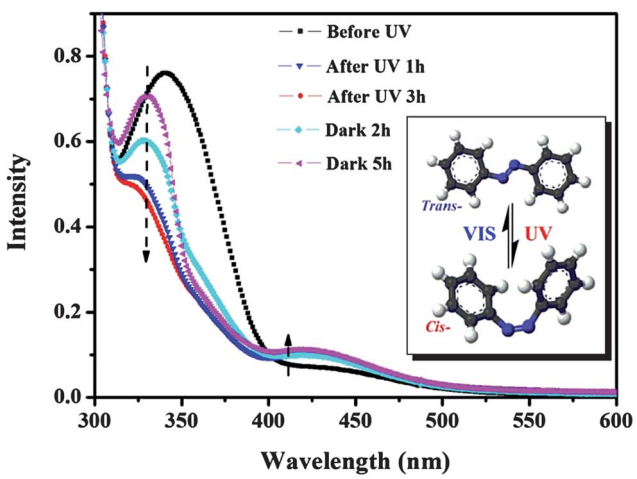


Fig. 2 UV-vis spectra of the U–PCL/Azo-benzene complex under UV 365 nm exposure before, and after dark treatment at room temperature.

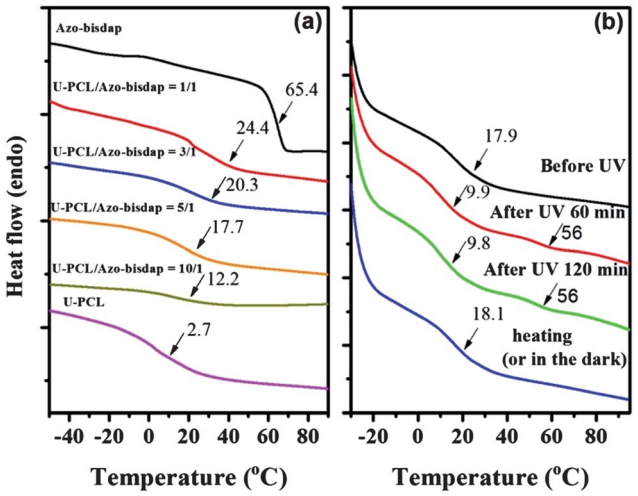


Fig. 3 (a) DSC curves of U–PCL samples containing various amounts of Azo-bisdap. (b) DSC curves of U–PCL/Azo-bisdap = 3/1 under UV 365 nm exposure before, after different times, and dark treatment.

homogenous phase. The T_g values of pure U–PCL and Azo-bisdap were 2.7 and 65.4 °C, respectively. As expected, all the blends show only one single T_g value, indicating that the uracil group of U–PCL is highly complementary to the diamidopyridine group of Azo-bisdap. Considering that the photo-isomerization of azobenzene is reversible and the *trans* and *cis*-isomers can be switched with UV and visible light, UV-induced isomerization and its reversibility were monitored in the film by DSC (Fig 3 (b)). Surprisingly, when the U–PCL/Azo-bisdap complex was irradiated with UV light, the U30–PCL/Azo-bisdap blend exhibits two T_gs at 9.9 and 56 °C, both lower than that of visible-light treatment, indicating the presence of micro-phase separation. The T_g at 55 °C comes from the amorphous phase of Azo-bisdap, implying that the hydrogen bonded dominant phase is excluded resulting in two T_gs. Based on the above discussion, the results suggest that the *cis–trans* isomerization can change the motion ability of the PCL matrix. However, the value of T_g returns to its original value after visible light exposure (or in the dark), suggesting that the supramolecular complexes are photo-reversible in the bulk state. FTIR spectroscopy was also employed to investigate the phase transitions of the U–PCL/Azo-bisdap complex during the UV exposure period (Fig. S7†). After 3 h of UV exposure, the peaks at 3143 and 3210 cm^{-1} corresponding to N–H stretching of the bound shifted to higher wavenumber and the free amide N–H stretching vibration at 3300–3450 cm^{-1} appears gradually for a 3/1 U–PCL/Azo-bisdap blend in Fig. S7,† implying that a significant reduction in the fraction of association occurs in the hydrogen bonds between uracil and diamidopyridine. As mentioned in our discussion above of the DSC data, the FTIR results also revealed that the formation and disassociation of cross-linking points during the exposure process was probably the most important factor resulting in stable phase transitions.

Supramolecular binding motifs show giant vesicular aggregates due to the biocomplementary hydrogen bonding recognition (such as thymine and diacryldiamidopyridine functionalities).[8,13] Similar structures are expected to be present in the polymer networks; the morphology of supramolecular networks was investigated with atomic force microscopy (AFM) in the tapping mode regime. The thin film of the U–PCL/Azo-bisdap blend prepared by the solution-casting method on the glass substrate exhibits irregular island domains with lateral dimensions ranging from *ca* 300 to 800 nm (Fig. 4). Notably, the morphology of the film was significantly altered upon irradiation with UV light at 365 nm, as can be seen in Fig. 4 (b). A great number of hills on the surfaces provide evidence for the formation of the *cis* state as a consequence of irradiation with UV light. The root mean square (rms) roughness changed from 4.4 nm before irradiation to 20.9 nm after irradiation in this system. Similar morphological changes were reported for asymmetrical poly(vinyl alcohol)-*co*-ethylene membranes blended with azobenzene polymers.[14] Then this sample was stored in the dark for 3 h; the morphology of the surface was restored (Fig. 4 (c)) and the value of rms roughness returned to 4.2 nm. This result further demonstrated that the topological properties of the hydrogen bond network serving as a direct pathway for light irradiation led to a marked transformation in the surface roughness. Based on DSC and AFM results, the *cis*-formed U–PCL/Azo-bisdap complex exhibits an obvious change of rms (from 4.4 to 20.9 nm^{-1}) corresponding to its phase separation regime as shown in Fig. 4b, indicative of unspecified structural features at a relatively large size. On the other hand, the formation of the *cis* isomer results in the increase of the intermolecular steric effect between azo-dye molecules and the

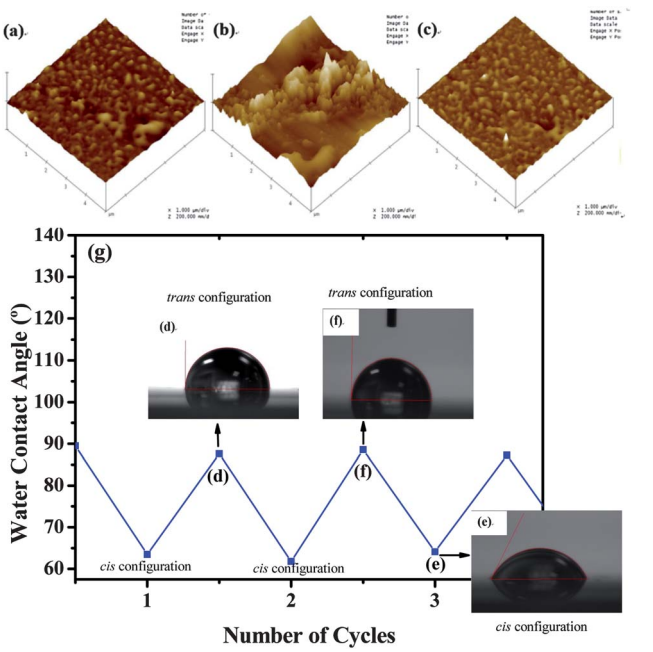


Fig. 4 AFM images of the U–PCL/Azo-bisdap complex and photographs of the water droplet shape on the U–PCL/Azo-bisdap complex before irradiation (a and d), after irradiation with UV light (b and e), and after UV irradiation followed by 3 h of exposure to visible light (c and f). (g) Reversible wettability transitions of the U–PCL/Azo-bisdap complex after several cycles of irradiation: 3 h at $\lambda = 354$ nm followed by 3 h at $\lambda > 420$ nm.

formation of a physical network of these domains. Similar results were verified in contact angle (CA) measurements of U–PCL/Azo-bisdap. The samples showed the most significant static CA change; the CA of U–PCL/Azo-bisdap decreased from 89.8° to 63.5° upon UV irradiation. Wettability can be switched back to its initial hydrophobic state after exposure to visible-light for 3 h. These phenomena were repeated four times with the same results (Fig. 4 (g)). This behavior arose presumably because the *trans*-to-*cis* isomerization of azobenzene induced by UV light irradiation leads to a large increase in the dipole moment of this molecule.[2] More interestingly, significant size changes of the aggregates were observed in the UV-exposed U–PCL/Azo-bisdap complex over 60 min at ambient temperature, and *cis*-to-*trans* isomerization proceeded over a one-day period (Fig. S6†). This morphological change can be explained in terms of an increase in the torsional strain upon isomerization of *trans*-azobenzene into the less planar (sterically bulky) *cis*-isomer.[2a,14] According to all the above, these results provide strong direct evidence of higher hydrophilicity from the UV-exposed sample than the visible light-exposed sample. Thus, we confirm that the major fraction of intermolecular *trans*-isomers existed after irradiation with UV light. In addition, this study demonstrates a simple yet effective approach to tune the properties of surfaces using noncovalent interactions, thus providing a potential route toward design and manipulation of hydrophilic/hydrophobic patterns.

Conclusions

In summary, dye-doped polymer materials are obtained by simply mixing nucleobase-functionalized polymers with DAP-modified chromophores. The photoresponsivity of the supramolecular complexes was confirmed by the occurrence of the UV and visible light-induced reversible *trans–cis* photoisomerization. The isomerization produces large structural changes in the azobenzene conformation and significantly affects its thermal properties, which is the key to the unique photocontrollable behaviors in azobenzene-containing supramolecular systems. Thus, the wettability of the surface can be successfully controlled by alternating illumination with UV and visible light. This U–PCL/Azo-bisdap supramolecular system by an external stimulus may open the way to many potential applications, including self-healing paint, chemical lithography, and nonlinear optical systems.

Acknowledgements

This study was supported financially by the National Science Council, Taiwan (contract no. NSC-102-2221-E-110-082).

Notes and references

1 (*a*) Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature*, 1990, **347**, 658; (*b*) Z. Sekkat and M. Dumont, *Appl. Phys. B: Lasers Opt.*, 1992, **54**, 486; (*c*) S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777; (*d*) K. G. Yager and C. J. Barret, *J. Photochem. Photobiol., A*, 2006, **182**, 250.

2 (*a*) G. S. Kumar and D. C. Neckers, *Chem. Rev.*, 1989, **89**, 1915; (*b*) S. Hvilsted, F. Andruzzi, C. Kulinna, H. W. Siesler and P. S. Ramanujam, *Macromolecules*, 1995, **28**, 2172; (*c*) H. M. D. Bandarab and S. C. Burdette, *Chem. Soc. Rev.*, 2012, **41**, 1809.

3 (*a*) C. Guzman-Verri, L. Manterola, A. Sola-Landa, A. Parra, A. Cloeckaert, J. Garin, J. P. Gorvel, I. Moriyon, E. Moreno and I. Lopez-Goni, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 12375; (*b*) M. Alemani, M. V. Peters, S. Hecht, K. H. Rieder, F. Moresco and L. Grill, *J. Am. Chem. Soc.*, 2006, **128**, 14446; (*c*) A. Szilagyi, K. Sumaru, S. Sugiura, T. Takagi, T. Shinbo, M. Zrinyi and T. Kanamori, *Chem. Mater.*, 2007, **19**, 2730.

4 (*a*) C. F. Huang, W. Chen, T. P. Russell, A. C. Balazs, F. C. Chang and K. Matyjaszewski, *Macromol. Chem. Phys.*, 2009, **210**, 1484; (*b*) M. Chen and F. Besenbacher, *ACS Nano*, 2011, **5**, 1549.

5 B. Y. Choi, S. J. Kahng, S. Kim, H. Kim, H. W. Kim, Y. J. Song, J. Ihm and Y. Kuk, *Phys. Rev. Lett.*, 2006, **96**, 156106.

6 (*a*) J. M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, 1995; (*b*) I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692; (*c*) R. P. Sijbesma and E. W. Meijer, *Chem. Commun.*, 2003, 5; (*d*) S. Sivakova and S. J. Rowan, *Chem. Soc. Rev.*, 2005, **34**, 9; (*e*) K. Yamauchi, A. Kanomata, T. Inoue and T. E. Long, *Macromolecules*, 2004, **37**, 3519.

7 (*a*) E. A. Archer and M. J. Krische, *J. Am. Chem. Soc.*, 2002, **124**, 5074; (*b*) D. R. Vutukuri, S. Basu and S. Thayumanavan, *J. Am. Chem. Soc.*, 2004, **126**, 15636.

8 (*a*) S. Rieth, C. Baddley and J. D. Badjic, *Soft Matter*, 2007, **3**, 137; (*b*) T. Aida, E. W. Meijer and S. I. Stupp, *Science*, 2012, **335**, 813.

9 (*a*) R. Hoogenboom, D. Fournier and U. S. Schubert, *Chem. Commun.*, 2008, 155; (*b*) A. J. Wilson, *Soft Matter*, 2007, **3**, 409; (*c*) A. Bertrand, F. Lortie and J. Bernard, *Macromol. Rapid Commun.*, 2012, **33**, 2062.

10 (*a*) C. C. Cheng, C. F. Huang, Y. C. Yen and F. C. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6416; (*b*) C. C. Cheng, Y. C. Yen, Y. S. Ye and F. C. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6388.

11 (*a*) I. H. Lin, C. C. Cheng, Y. C. Yen and F. C. Chang, *Macromolecules*, 2010, **43**, 1245; (*b*) J. H. Wang, C. C. Cheng, Y. C. Yen, C. C. Miao and F. C. Chang, *Soft Matter*, 2012, **8**, 3747; (*c*) I. H. Lin, C. C. Cheng, C. W. Huang, M. C. Liang, J. K. Chen, F. H. Ko, C. W. Chu, C. F. Huang and F. C. Chang, *RSC Adv.*, 2013, **3**, 12598; (*d*) I. H. Lin, C. C. Cheng, W. T. Chuang, J. K. Chen, U. S. Jeng, F. H. Ko, C. W. Chu, C. F. Huang and F. C. Chang, *Soft Matter*, 2013, **9**, 9608.

12 (*a*) L. Fielding, *Tetrahedron*, 2000, **56**, 6151; (*b*) N. Mesplet, P. Morin and J. P. Ribet, *Eur. J. Pharm. Biopharm.*, 2005, **59**, 523.

13 R. J. Thibaul, P. J. Hotchkiss, M. Gray and V. M. Rotello, *J. Am. Chem. Soc.*, 2003, **125**, 11249.

14 B. Tylkowski, S. Peris, M. Giamberini, R. Garcia-Valls, J. A. Reina and J. C. Ronda, *Langmuir*, 2010, **26**, 14821.