Polymer Design

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One is Enough: Influencing Polymer Properties with a Single Chromophoric Unit**

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Designing a polymer usually involves the incorporation of multiple functional units into a polymer chain, which mutually determine the polymer properties. By combining various functional units, a myriad of polymer properties can be fine-tuned. Classical polymer chemistry teaches us that a single functional group—in particular the end-group of a polymer chain—does not contribute to the polymer properties, as is indeed true in most cases. However, nature tells us a different story. The photoisomerization of a single retinal molecule inside a large polymeric complex called rhodopsin is the mechanism for the highly sensitive ocular system found in vertebrate photoreceptors. The conversion of the 11-*cis* isomer into the all-*trans* isomer results in a change in the higher-order structure of the rhodopsin unit.[1]

The use of light has been a long-standing practice in polymer science that has led to numerous applications, ranging from nonlinear optical materials, optical datastorage, organic light-emitting diodes, and photovoltaics to lithographic processes.[2] Recently, the idea of stimulating a single chromophore on a polymer chain and amplifying its effect through the polymer chain has motivated the evolution of new exciting research areas in polymer science. To attain such high synthetic precision, it is crucial to choose not only an appropriate chromophoric unit that shows reversible or irreversible changes, but also synthetic routes that enable the attachment of a single dye to one polymer chain. Recent examples of influencing polymeric properties either in the bulk or in solution phases by using a single chromophore and emerging applications of this approach are summarized herein.

It is possible to place a single chromophoric unit at a defined position within a polymer chain owing to the recent development of controlled polymerization techniques, in particular controlled radical polymerization techniques. Evans and co-workers showed that the photochromism of the dye can be maintained and the local environment surrounding each individual dye molecule controlled by the incorporation of a single photochromic dye in a single polymer chain. They synthesized mid- and end-functionalized 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyran–poly(*n*-butyl acrylate) conjugates by atom-transfer radical polymerization (ATRP) and demonstrated that the placement of the naphthopyran photochromic dye in the middle of poly(*n*-butyl acrylate) chains with a low glass-transition temperature led to faster secondary decoloration than that observed upon end placement.[3]

The achievement of a response from a polymer upon external stimulation has fascinated polymer scientists.[4] One particular interest concerns reversible morphological changes of nanostructures in solution.[5] Such behavior is often triggered by changes in the pH value, temperature, or light. However, one question arises: is a single chromophoric unit enough to influence this responsive behavior? Recent studies have shown that the incorporation of a single chromophoric unit in a polymer chain can induce sufficient changes in the properties of the polymer. Pioneering studies on light-induced structure changes in solution were carried out by Fréchet and co-workers, who synthesized a functional amphiphile consisting of a poly(ethylene glycol)–lipid conjugate and a single 2-diazo-1,2-naphthoquinone (DNQ) moiety attached to the end of the hydrophobic tail (P1 in Scheme 1).[6] DNQ is a commonly used chromophoric unit owing to its photoinduced Wolff rearrangement, which results in a dramatic change in solubility. It is therefore used intensively for industrial photoresists.[7] Interestingly, this Wolff rearrangement can be triggered not only by UV irradiation but also by a two-photon absorption.[8] In the nonirradiated state, the functional amphiphile forms micelles in solution. However, upon irradiation either with UV light at 350 nm or with a pulsed laser at 795 nm (to induce a two-photon absorption), a change

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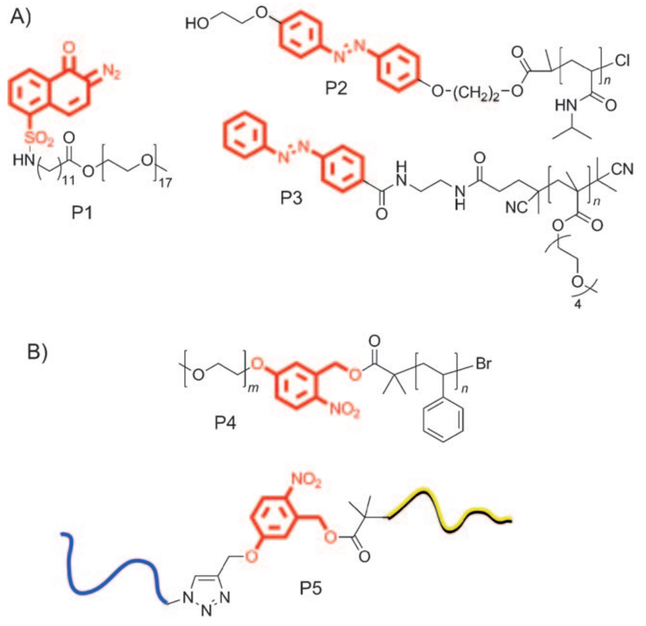

Scheme 1. a) Polymer structures containing one dye to control solution properties. b) Block-copolymer structures with a photocleavable junction based on an *o*-nitrobenzyl ester.

in the amphiphilic properties of the molecule leads to the destruction of the micelles.

Another class of stimuli-responsive polymers is temperature-responsive polymers, which undergo a phase transition upon heating or cooling. One example is poly(*N*-isopropylacrylamide) (PNIPAM), which features a lower critical solution temperature (LCST) in water of 32 °C.[9] The solubility of polymers in water depends on two antagonizing factors: 1) the hydrogen bonding between H_2O molecules and polar groups of the polymer and 2) the hydrophobic effect due to a better reorganization of H_2O molecules around nonpolar groups of the polymer; these effects result in a negative enthalpy change counterbalanced by a negative entropy change. Thus, marginal changes, especially of nonpolar groups, within the polymer chain can have a dramatic effect at temperatures close to the LCST because this phase separation is mainly entropically driven.[9] Accordingly, the combination of light and temperature as stimuli to induce local changes in polarity has gained significant attention. Several examples of the incorporation of chromophoric moieties into polymers and the potential of light as a stimulus have been reported.[10]

In contrast, the ability of a light stimulus to trigger morphological changes in the nanostructure of a temperature-responsive polymer containing a single chromophoric unit has not been investigated extensively. Akiyama and Tamaoki used an azobenzene derivative substituted with a 2-chloropropionyl group as an initiator for the ATRP of *N*-isopropylacrylamide (NIPAM).[11] They synthesized a series of PNIPAM polymers with degrees of polymerization (DP) varying between 14 and 93 ($M_w/M_n < 1.1$), all of which featured a single azobenzene unit at the α-chain end (P2 in Scheme 1). Polymers with a smaller DP, that is, a higher azobenzene content, showed a decreased cloud point with the *trans* isomer of azobenzene when compared to unmodified PNIPAM. However, the azobenzene content did not significantly affect the cloud point upon UV irradiation to yield the *cis* isomer. It was therefore concluded that the *cis* isomer had hydrophilicity similar to that of the NIPAM unit. Impressively, cloud-point shifts upon irradiation of up to 12 °C were possible with a single azobenzene unit per polymer chain. Similarly, Jochum et al. demonstrated that temperature-responsive poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) with DP values of 14 and 29 and a single azobenzene end group (P3 in Scheme 1) underwent a reversible light- and temperature-controlled phase transition in water.[12] Higher values for the cloud points were measured after UV irradiation of the aqueous polymer solutions owing to the higher polarity of *cis*-azobenzene.

Besides the use of a single chromophore to tune the solution properties of polymers, applications in the bulk have been an emerging area. Block copolymers have recently been used to prepare nanoporous thin films for nanopatterning, separation membranes, and sensors. Crucial for the preparation of nanoporous thin films is the selective removal of one block domain—usually the minor domain in a cylindrical morphology—under mild conditions. Degradation under harsh conditions, such as deep UV irradiation of a poly(methyl methacrylate) (PMMA) block or the use of an acid-sensitive linker, has been explored. Kang and Moon broke new ground by using a photocleavable *ortho*-nitrobenzyl (ONB) linker within a polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymer P4 in Scheme 1).[13] Cleavage upon irradiation with UV light (350 nm, 6 h) was shown to be successful not only in solution but also within thin films of a vertically aligned cylindrical morphology. Simple washing with methanol/water resulted in a nanoporous PS film (see Figure 1).

Fustin and co-workers extended the synthetic strategy to a series of block copolymers featuring a single photocleavable ONB junction.[14] By using an ATRP initiator including the ONB photocleavable junction and an alkyne group to enable a simultaneous copper(I)-catalyzed azide–alkyne cycloaddition, they prepared a series of different diblock copolymers (P5 in Scheme 1), such as PEO-*b*-PS, PEO-*b*-PtBA (tBA = *tert*-butyl acrylate), and PS-*b*-PMMA, with varying block lengths while maintaining narrow polydispersities ($M_w/M_n < 1.2$). Photocleavage of the diblock copolymers by UV light ($\lambda = 300$ nm) was demonstrated for PEO-*b*-PS in solution to be complete after 15 min, as proven by size-exclusion chromatography.

Nojima et al. used a photocleavable diblock copolymer to investigate the crystallization and crystal orientation of poly(ε-caprolactone) (PCL) in confined geometries.[15] They prepared a PCL-*b*-PS block copolymer with a photocleavable ONB junction and used shear to establish the preferential orientation of nanocylinders of PCL. The PCL crystal orientation was then investigated as a function of crystallization temperature (T_c) for both the nonirradiated sample, that is, the intact diblock copolymer, and the irradiated sample, that is, the photocleaved diblock copolymer. First, it was shown that the orientation of the nanocylinders was completely preserved in PCL/PS after irradiation. Second, for

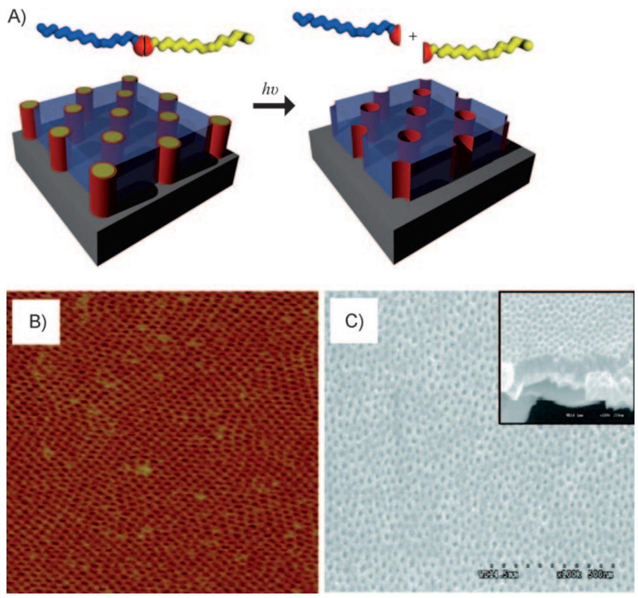

Figure 1. a) Schematic illustration of the use of photocleavable block copolymers as templates for the formation of nanoporous thin films. b) AFM image of a solvent-annealed thin film of PS-*b*-PEO featuring an ONB junction.[13] c) SEM image of the nanoporous PS film after photocleavage and rinsing with a solvent to selectively remove PEO domains.[13]

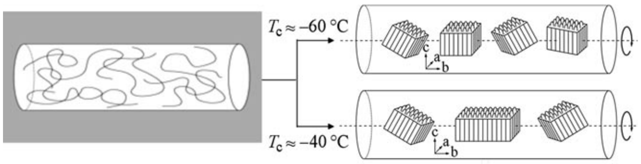

Figure 2. Schematic illustration showing the difference in the crystal orientation of the nanocylinders between PCL homopolymers crystallized at −60 and −40 °C.[15]

both the nonirradiated and the photocleaved samples, the *b* axis of the unit cell of PCL crystals was preferentially oriented parallel to the long axis of the nanocylinders. Notably, the degree of crystal orientation increased with increasing crystallization temperature only for the photocleaved sample, that is, for nontethered PCL chains (Figure 2).

In summary, recent developments have successfully shown that the careful use of a single chromophore on methodically designed polymers can indeed be sufficient to tune polymer properties upon irradiation. Nevertheless, continued research is necessary to further explore possible applications as well as to enhance the time response of the polymeric systems. Irradiation times of hours in most cases are far from desirable. Nature has taught us that more is possible!

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[1] K. Palczewski, T. Kumasaka, T. Hori, C. A. Behnke, H. Motoshima, B. A. Fox, I. Le Trong, D. C. Teller, T. Okada, R. E. Stenkamp, M. Yamamoto, M. Miyano, *Science* **2000**, *289*, 739 – 745.
[2] N. S. Allen, *Handbook of Photochemistry and Photophysics of Polymeric Materials*, Wiley, New York, **2010**.
[3] N. Malic, J. A. Campbell, R. A. Evans, *Macromolecules* **2008**, *41*, 1206 – 1214.
[4] M. A. Cohen Stuart, W. T. S. Huck, J. Genzer, M. Müller, 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.
[5] A. O. Moughton, J. P. Patterson, R. K. O'Reilly, *Chem. Commun.* **2011**, *47*, 355 – 357.
[6] A. P. Goodwin, J. L. Mynar, Y. Ma, G. R. Fleming, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2005**, *127*, 9952 – 9953.
[7] W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2193 – 2256.
[8] N. K. Urdabayev, V. V. Popik, *J. Am. Chem. Soc.* **2004**, *126*, 4058 – 4059.
[9] H. G. Schild, *Prog. Polym. Sci.* **1992**, *17*, 163 – 249.
[10] J.-M. Schumers, C.-A. Fustin, J.-F. Gohy, *Macromol. Rapid Commun.* **2010**, *31*, 1588 – 1607.
[11] H. Akiyama, N. Tamaoki, *Macromolecules* **2007**, *40*, 5129 – 5132.
[12] F. D. Jochum, L. zur Borg, P. J. Roth, P. Theato, *Macromolecules* **2009**, *42*, 7854 – 7862.
[13] M. Kang, B. Moon, *Macromolecules* **2009**, *42*, 455 – 458.
[14] J.-M. Schumers, J.-F. Gohy, C.-A. Fustin, *Polym. Chem.* **2010**, *1*, 161 – 163.
[15] S. Nojima, Y. Ohguma, K.-I. Kadena, T. Ishizone, Y. Iwasaki, K. Yamaguchi, *Macromolecules* **2010**, *43*, 3916 – 3923.