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Temperature- and light-responsive smart polymer materials†

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Stimuli-responsive polymers have been attracting great interest within the scientific community for several decades. The unique feature to respond to small changes in the environmental conditions has made this class of materials very promising for several applications in the field of nanoscience, nanotechnology and nanomedicine. So far, several different chemical, physical or biochemical stimuli have been investigated within natural or synthetic polymers. Very interesting and appealing seems to be the combination of several stimuli to tune the properties of these materials in manifold ways. Within this present review, we want to highlight the recent progress in the field of synthetic stimuli-responsive polymers combining temperature and light responsiveness.

Introduction

Stimuli-responsive polymers, also called ''smart materials'' have raised great interest in natural science within the last few decades.[1–4] Such materials are conventionally (macro)-molecules that undergo changes in response to small external variations in environmental conditions.[5] These systems opened

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access to promising applications in the field of nanomedicine like affinity separations, immunoassays, enzyme recovery and drug delivery.[6]

In general, several classes of stimuli-responsive polymers have been reported. Polysaccharides, proteins and nucleic acids represent one huge group of stimuli-responsive biopolymers that can be found widely in a living environment.[5] Indeed, these materials belong to the oldest class of substances in Nature having stimuli-responsive properties. However, for several years, the class of synthetic polymers with stimuli-responsive properties has attracted the same or even greater attention within the scientific community.[7]

The number of scientific contributions on synthetic stimuli-responsive polymers has increased exponentially within the last two decades.[8] This is mainly due to the fact that new methods for the polymerization of functional monomers have been developed. In this context, controlled radical polymerization techniques such as the nitroxide-mediated polymerization (NMP),[9] the atom transfer radical polymerization (ATRP)[10] and the reversible addition–fragmentation chain transfer (RAFT) polymerization[11] have been used intensively. In fact, all these polymerization methods show a high tolerance towards functional groups while providing the benefit to result in polymers and block copolymers with a narrow molecular weight distribution and defined end-groups. Furthermore, the new synthetic strategies in polymer analogous reactions[12] – also called post-polymerization modifications[13] – of polymeric precursors *via* ''click'' chemistry[14] have proved to be highly attractive tools to introduce certain functional groups into a polymer. Thus, huge classes of defined synthetic materials, such as stimuli-responsive polymers were prepared having a large variety of functionalities.

In principle, stimuli-responsive materials can be considered as soft materials and furthermore, they have very important features in common: they respond either to (a) chemical stimuli, (b) physical stimuli or (c) biochemical stimuli in solid state, in solution or as gel.[5] With regard to chemical stimuli, changes in the pH value[15,16] and in the ionic strength,[17] as well as the addition of chemical agents, *e.g.* solvents[18] or gases[19] and redox-reactions[20] should be mentioned here as representing probably the most common examples of chemical stimuli. They have found broad application in the area of materials science nowadays.[7]

As far as physical stimuli are concerned, voltage[21] and temperature changes,[5,22,23] light-irradiation,[24–26] or mechanical stress[27–29] are, indeed, very important and promising physical stimuli in responsive systems. In this context, it is worth noting that biochemical stimuli have been recognized as a third category of stimuli that involve responses to antigens, enzymes, ligands or other biochemical agents.[5]

Of all stimuli-responsive polymers, temperature-responsive polymers probably belong to one of the largest classes and their unique and characteristic property to feature a lower critical solution temperature (LCST) has been studied intensely in recent decades.[5,22,23] The LCST is a fascinating phenomenon found for various polymer solutions. Often polymer solutions exhibit both a LCST and an upper critical solution temperature (UCST). For the LCST, at temperatures below the LCST the polymer is completely miscible in the solvent in all proportions, whereas at temperatures above the LCST a phase separation occurs. Particularly exciting is the LCST of some water soluble polymers, which tend to phase-separate from solution upon heating. In fact, the most investigated temperature-responsive polymer featuring a LCST in water is the poly(*N*-isopropylacrylamide) (PNIPAM). The LCST of PNIPAM was reported to be around 32 °C, which is close to the human body temperature.[23] This feature made this polymer very promising for *e.g.* drug delivery applications. Consequently, by altering the temperature of PNIPAM solution in water, its solubility behaviour can be changed from hydrophilic (soluble) to hydrophobic (insoluble) and *vice versa* and can, thus, be triggered externally. Research in the field of thermo-responsive polymers has focused intensely on PNIPAM. However, other *N*-substituted polyacrylamides[30,31] and other classes of polymers such as poly(oligoethyleneoxide-(meth)acrylate)s[32] or poly(2-oxazoline)s[33] exhibit a LCST as well.

Besides the aforementioned temperature as a physical stimulus, light has equally attracted attention in the field of stimuli-responsive polymers. Light has the specific physical characteristic that it can be localized in time and space.[26] For this reason, it has been used as a trigger to release encapsulated substances in light-responsive block copolymer micelles, as demonstrated by Matyjaszewski and coworkers.[34] Light-responsive polymers and block copolymers have recently been reviewed by the groups of Zhao[24,35] and Gohy.[26] One should note that even one light-responsive unit can be sufficient to influence the properties of the whole polymer chain within a light-responsive polymer system.[36]

In general, a light-responsive behaviour can either be reversible or irreversible, depending on the chromophore that is attached to the polymeric backbone or to the chain end. Most commonly, photochromic molecules are used to tune the properties within light-responsive polymers.[37] These well-known organic dyes undergo a reversible isomerisation upon irradiation. This process is usually accompanied with a polarity change as well as a colour change in the chromophoric units. Such phenomena can be observed in chemical compounds like azobenzene, spiropyran, salicylideneaniline *etc.* Consequently, a light-responsive polymer containing photochromic units would change its solubility reversibly through an irradiation process as long as the irradiation is being applied. The isomerisation of a photochromic unit can usually be followed by a thermal or visible re-isomerization process. UV-light in the range between 300 and 400 nm is generally used for the light-stimulation, whereas visible light (λ > 400 nm) is used for the initiation of the re-isomerization process.

An irreversible light-responsive behaviour can generally be observed in polymers having photocleavable units instead of photochromic units. Upon irradiation, the light-responsive moiety of the corresponding polymer would then be cleaved into a more polar species through an irreversible transformation.[26] As one example, the *o*-nitrobenzyl ester (ONB)[38–43] should be mentioned here as constituting probably the most important chromophores featuring an irreversible light-responsive behaviour. The photocleavage reaction is generally initiated by UV-light; however, under certain conditions, NIR-light can be used for cleavage of ONB-groups as well.[42] In some other cases, the term of light-responsiveness in polymeric systems can be extended to reversible or irreversible cross-linking reactions based on coumarin dimerization.[26]

In recent years, various stimuli-responsive polymer systems have been reported and were often combined to yield dual or even multi-responsive polymers.[44,45] These materials have attracted notable interest in academia as they allow tuning of their properties in multiple ways. In particular, temperature-responsive polymers have been combined with light-responsive chromophores to give temperature- and light- responsive polymers.

In this present review, we want to emphasize recent developments in the field of synthetic water soluble polymers, combining both stimuli mentioned: temperature and light. We will focus on examples that allow for a fine-tuning of the LCST by irradiation or enable the controlled formation of nanoaggregates by combining temperature and light. This correlates to the previous scientific work of several research groups. In addition, we will mention other aspects and suitable applications in the area of temperature- and light-responsive polymers.

Thermoresponsive polymers containing azobenzene

Statistical copolymers and end-group functionalized homopolymers

The azobenzene chromophore was recognized from early on as a suitable photochromic molecule to influence the polarity within a polymer upon light-irradiation in a reversible manner.[26,46] In fact, azobenzene shows the fascinating property to undergo photo-isomerization from *trans* to *cis* and *vice versa*, depending on the irradiation wavelength.[47] It is remarkable to note that this isomerization process is accompanied by a strong polarity change in the photochromic unit. This polarity change is a direct consequence of the change in the dipole moment from 0 Debye for the *trans*-isomer to 3 Debye for the *cis*-isomer.[48] For this reason, the azobenzene chromophore plays a major role in temperature- and light responsive polymers.

To the best of our knowledge, the first example of a temperature- and light-responsive polymer was reported by Kungwatchakun and Irie in 1988.[49] They synthesized copolymers by polymerization of *N*-isopropylacrylamide (NIPAM) with *N*-(4-phenylazophenyl)acrylamide. The intention of their work was to photo-control the phase separation temperature of aqueous solutions of PNIPAM by introducing photochromic azobenzene moieties. Consequently, a shift in the phase separation temperature, *i.e.* the LCST, from initially 21 °C to 27 °C after UV-light irradiation was found for a copolymer system containing 2.7 mol% azobenzene groups. This change was explained by the change in the dipole moment that is due to the *trans*-to-*cis* isomerisation of the azobenzene moieties. The initial phase transition temperature of 21 °C was re-obtained after exposure to visible light. Noteworthily, Kungwatchakun and Irie found that there exists a direct correlation between the light-induced shift of the phase transition temperature and the amount of azobenzene incorporated into the copolymer. According to their investigations, the phase separation temperature depends on the balance between the hydrogen bond formation ability of the polymer surrounded with water and the intermolecular hydrophobic forces. At higher azobenzene concentrations incorporated into the copolymer, the hydrophobic property change was not high enough to weaken the existing intermolecular interacting forces and, consequently, the phase transition temperature remained constant upon UV-light irradiation.[50,51]

Several years later, research on the reversible photo-control of the LCST was continued. Menzel and coworkers reported in 1994 the synthesis of copolymers of *N*,*N*-dimethylacrylamide (DMA) and 4-phenylazophenyl acrylate. Their intention was to increase the temperature gap of the LCST between a non-irradiated and an irradiated copolymer dissolved in water.[52] They found that the photo-isomerization of the azobenzene moieties of the copolymers was comparable with that in solutions of azobenzene unimers as measured by UV/Vis spectroscopy. The obtained values for the cloud points decreased with increasing content of azobenzene in the copolymer system. This was explained by the hydrophobic nature of the aromatic azobenzene dye, similar to the PNIPAM copolymer of Kungwatchakun and Irie. Furthermore, Menzel and coworkers measured a shift of the phase transition temperature up to 14 °C, corresponding to the difference between the cloud points of the non-irradiated and the irradiated DMA copolymers having an average amount of 7.3 mol% azobenzene moieties.

In 2001, Sugiyama and Sono found that copolymers originating from *N*-(2-hydroxypropyl)methacrylamide (HPMA) with a certain ratio of azobenzene acrylate monomers exhibit also a LCST in aqueous solution.[53] It was found that the LCST as measured in the photostationary state showed a temperature that was 2–4 °C higher compared to that in the dark state.

An interesting application for a light control of the LCST was reported by Hoffman and Stayton.[54] They demonstrated that photo-induced changes in the size and hydration of a polymer chain can be used to regulate substrate access and enzyme activity of the enzyme endoglucanase 12A (see Fig. 1). For this purpose, a temperature- and light-responsive copolymer based on DMA with azobenzene moieties was synthesized by radical copolymerization in the presence of a functional chain transfer agent to enable a subsequent enzyme–polymer conjugation. This ''smart'' polymer acted as an antenna that reversibly responded to light at different wavelength, thus allowing to switch on and off the activity of the polymer–enzyme conjugates. The LCST behaviour of the copolymer under UV and visible light irradiation was investigated as well. Hoffman and Stayton found a similar responsive behaviour for the photo-control of the cloud points as previously reported by Menzel and coworkers. These results have further been used for a controlled stimulation of a polymer–streptavidin conjugate.[55]

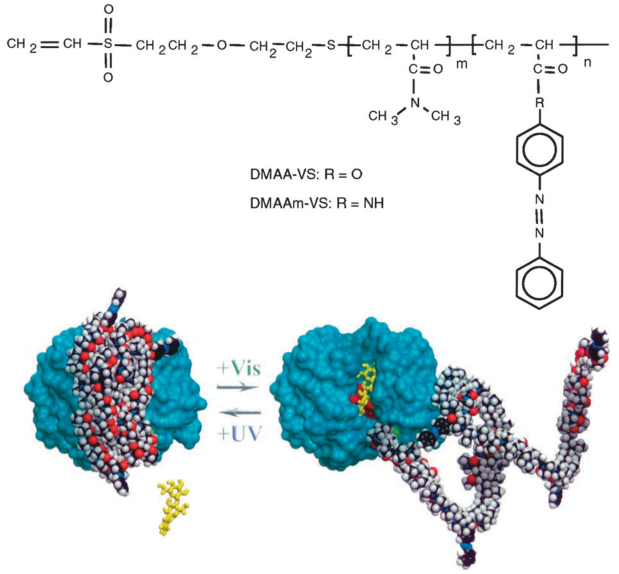


Fig. 1 Schematic model of the photo-responsive enzyme switch using a temperature- and light-responsive copolymer. Adapted from ref. 54 with permission from the Proceedings of the National Academy of Sciences (PNAS), copyright by the National Academy of Sciences.

The research on temperature- and light-responsive polymers with azobenzene moieties was further intensified by Akiyama and Tamaoki.[56] They copolymerized NIPAM with different amounts of azobenzene-bearing acrylamide monomers. A photo-control of the phase transition temperature was observed, which was explained by the isomerisation of the azobenzene attached to the polymer. Consequently, these polymers exhibited an alternation of the LCST upon irradiation with UV and visible light. Furthermore, the authors investigated the properties of ''smart'' copolymer films. A change in the photo-induced wettability through contact angle measurements was reported for certain temperatures.

Several other investigations on PNIPAM-based copolymers using azobenzene as a chromophore to photo-control the phase transition temperature have been performed by the group of Freitag.[57] They proposed a new synthetic route towards the synthesis of photo-responsive NIPAM co-telomers. For this purpose, a polymeric precursor of PNIPAM containing reactive succinimide co-monomers was prepared. This precursor was converted with (3-aminopropyloxy)azobenzene in a polymer analogous reaction yielding a PNIPAM containing azobenzene copolymer. The solution properties of the copolymers in water were studied by turbidimetry and microcalorimetry. In good agreement with other research groups, the investigators found that the temperature-induced phase transition of the azobenzene-containing copolymers can be controlled efficiently by alternating light irradiation.

The investigation on temperature- and light-responsive copolymer systems has inspired also the work of Theato and coworkers.[58] In 2009, Jochum *et al.* reported the synthesis of several copolymers based on the PNIPAM, poly(*N*-cyclopropylacryamide),[59] poly(*N*-ethyl-*N*-methylacrylamide)[60] and poly(*N*,*N*-dimethylacrylamide)[61] each with various amounts of azobenzene moieties incorporated. The aim of their study was to investigate the different thermo-responsive polyacrylamide systems with regard to the ability to photo-control the LCST by the attachment of azobenzene. As a synthetic tool, activated ester polymers were utilized as polymeric precursors that were synthesized in a defined molecular weight by RAFT-polymerization. The temperature- and light-responsive copolymers were then obtained *via* a polymer analogous reaction of the polymeric precursor with functional amines (see Fig. 2).

All copolymers featured a LCST in aqueous solution, which was strongly dependent on the amount of hydrophobic azobenzene, whereas higher values for the cloud points were measured after UV-irradiation, a phenomenon in agreement with the local polarity change in the irradiated azobenzene through the isomerization from *trans*-azobenzene to *cis*-azobenzene.

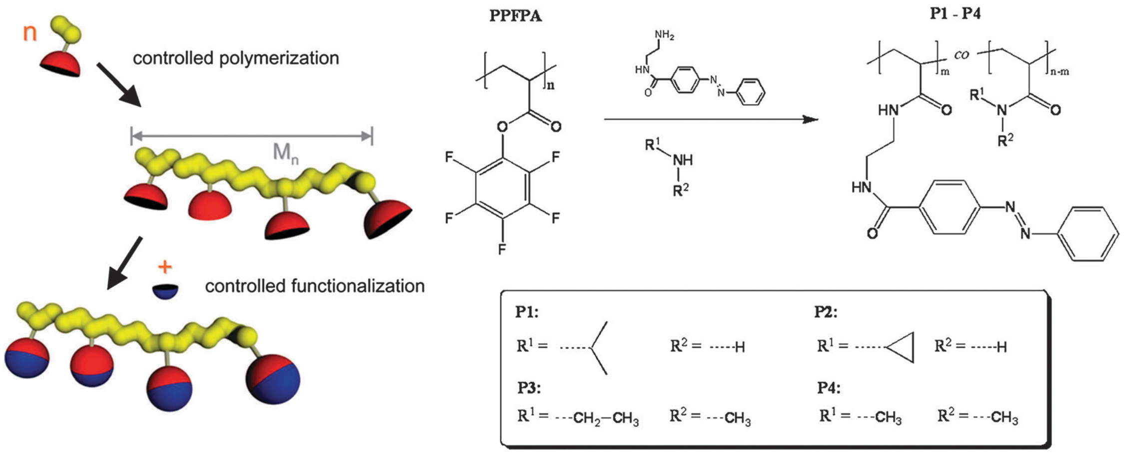


Fig. 2 Synthetic concept (left illustration) of a polymer analogous reaction of activated ester polymers to synthesize well-defined polymers. Reproduced in part from ref. 12 with permission from John Wiley and Sons. As an example, various temperature- and light-responsive polyacrylamides P1–P4 containing different amounts of azobenzene moieties were synthesized through a polymer analogous reaction of PPFPA polymers previously obtained from RAFT-polymerization (right scheme). Adapted from ref. 58 with permission from Elsevier.

The highest shift of the LCST was found for the copolymer of poly(*N*,*N*-dimethylacrylamide) containing 8.5 mol% of azobenzene groups. The copolymers were then employed in a reversible isothermal solubility change that was solely controlled by UV-irradiation at a fixed temperature slightly above the LCST.

Another exciting example to control the phase transition of PNIPAM using azobenzene as a light-responsive moiety was published by Akiyama and Tamaoki.[62] They synthesized an azobenzene-bearing initiator for the ATRP polymerisation of NIPAM. Consequently, the resulting polymers having different molecular weights and chain lengths possessed only a single terminal azobenzene end-group. The aqueous solution of these polymers displayed a LCST that could also be altered reversibly by light irradiation. The LCST shifts increased linearly up to a value of 10 °C with decreasing molecular weight, *i.e.* there was an increasing influence of the azobenzene end-group.

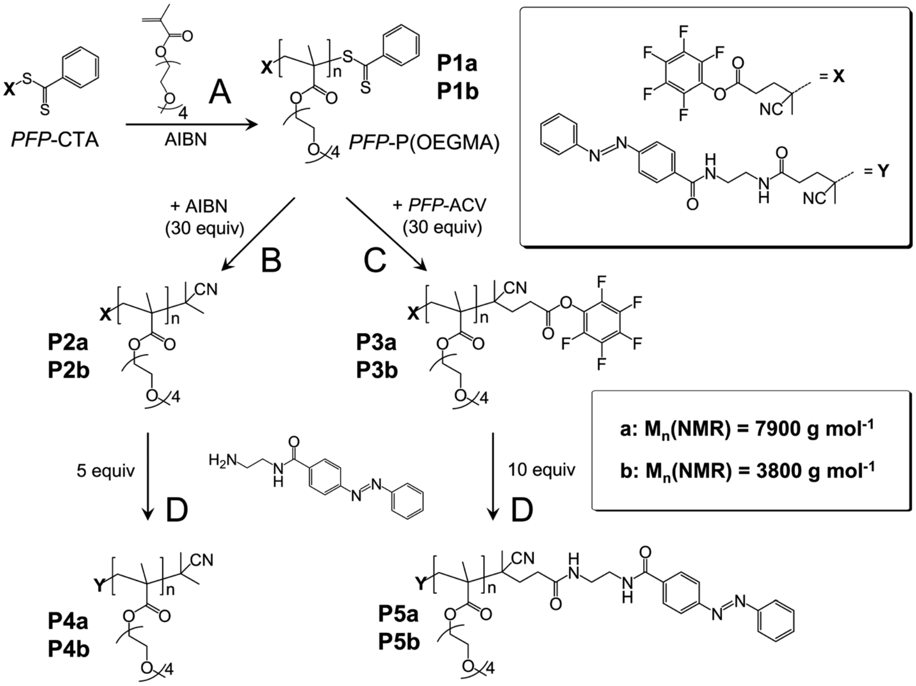
Inspired by the results of Akiyama *et al.*, the group of Theato investigated the influence of different end-groups upon the LCST[63] or the upper critical solution temperature (UCST)[64] of polymers based on poly(oligo(ethylene glycol) monomethyl ether methacrylate) [POEGMA] in water or alcohols, respectively. First, the influence of azobenzene end-groups upon the phase separation temperature of temperature-responsive POEGMA with a short chain length was investigated.[65] Via the RAFT polymerisation of the methacrylate monomers using an activated ester RAFT-reagent in combination with orthogonal end group functionalization the azobenzene could be installed at either chain ends (see Scheme 1). This RAFT-reagent, namely PFP-CTA (originating from a pentafluorophenyl ester modified chain transfer agent),[66] has further been established as a very useful tool for the synthesis of homo- and heterotelechelic functionalized (stimuli-responsive) polymers for several different applications.[67–70]

While the chemical nature of the end-group of a long polymer chain has normally no influence on the LCST of a high molecular weight temperature-responsive polymer, the end group influence becomes essential in the case of short chain polymers.[63,65] Again, the phase transition temperature could be photo-controlled by irradiation with UV-light, due to the *trans*-to-*cis* photo-isomerization of the azobenzene at the end groups. A linear increase in the LCST-shifts with increasing amounts of azobenzene per polymer chain was found, in good agreement with the previously mentioned work of Akiyama *et al.*

Within the last few years, research on the stimulation of the LCST using the photochromic azobenzene has been more and more intensified. The group of Matyaszewski has reported on the synthesis and characterization of molecular brushes prepared from 4-methacryloyloxy-azobenzene (MOAB) and 2-(dimethylamino)ethyl methacrylate *via* ATRP.[71] In accordance with previous examples, they confirmed that the LCST could be photo-controlled by UV-irradiation.

Living cationic copolymerization of 2-(2-ethoxy)ethoxyethyl vinyl ether (EOEOVE) and 4-[2-(vinyloxy)ethoxy]azobenzene (AzoVE) was performed to obtain thermo-responsive poly(vinylethers) with azobenzene side groups.[72] The obtained copolymers showed different cloud point temperatures before and after irradiation with UV-light. In this way, it had also been possible to control the phase separation at a fixed temperature by irradiation at specific wavelengths.

Recently, the Winnik and Ikeda group could show that the reversible photo-controlled phase separation of an azobenzene



Scheme 1 Synthetic concept for the synthesis of thermoresponsive POEGMA polymers having either azobenzene in a high quantity at either the α-end (P4a, P4b) or on both sides of the polymer chain, respectively (P5a, P5b). For the RAFT polymerization, a functional RAFT reagent ''PFP-CTA'' was used. Adapted from ref. 65 with permission from the American Chemical Society (ACS).

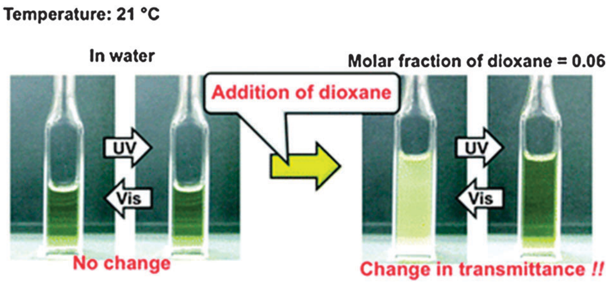


Fig. 3 UV-irradiation at room temperature of PNIPAM polymers with azobenzene end-groups in water/1,4-dioxane (6 mol% dioxane) reversibly converts a turbid suspension into a clear solution. Adapted from ref. 73 with permission from the Royal Society of Chemistry (RSC).

end-group functionalised PNIPAM polymer could be dramatically intensified through the addition of dioxane to water, which enabled the reversible conversion from a turbid suspension into a clear solution upon photo-irradiation (see Fig. 3).[73] In addition, the self-assembly of these polymers forming nanoparticles (R_H = 8 nm) in cold water as well as the photo-control of the phase transition temperature was studied.[74]

Another interesting example was reported by the research group of Watanabe.[75] They synthesized copolymers originating from 4-phenylazophenyl methacrylate and benzyl methacrylate monomers. In this study, the LCST of the copolymers in ionic liquids instead of water before and after UV-light irradiation was investigated. Furthermore, the UCST of PNIPAM copolymers with randomly distributed azobenzene groups P(AzoMA-*r*-NIPAm) in ionic liquids was investigated by Lodge and Watanabe as well.[76] They found that the UCST depends on the photoisomerization state of azobenzene, as well as on the azobenzene composition in the random copolymers (see Fig. 4). The UCST could be decreased by 43 °C by UV-light irradiation as measured by turbidimetry. Their work represents an excellent extension of previous investigations in which the LCST was always the focus of light-induced manipulations.

Zhao and coworkers used copolymers from *N*,*N*-dimethylacrylamide and *N*-4-phenylazophenyl acrylamide featuring a thiol end group to control the aggregation state of gold nanoparticles in aqueous solutions.[77] A similar copolymer was further used as a stabilizer for the synthesis of polyaniline nanoparticles,[78] as well as for the molecular recognition of α-cyclodextrin[79] or in polymer blends of the temperature-responsive Pluronic F127.[80]

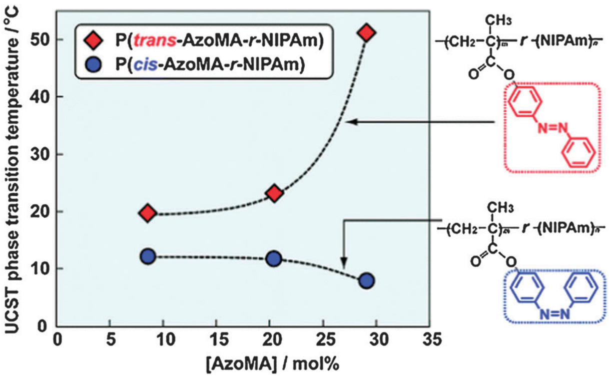


Fig. 4 Photo-control of the UCST in ionic liquids of P(AzoMA-*r*-NIPAm) copolymers. The UCST of P(AzoMA-*r*-NIPAm) depends on the isomerisation of the azobenzene state and on the amount of chromophores incorporated. Adapted from ref. 76 with permission from the American Chemical Society (ACS).

The behaviour of temperature-responsive polymers with azobenzene moieties has been studied intensively in solution as mentioned above. Furthermore, temperature-responsive polymers were investigated for host–guest complexation[81] and swelling behaviour applications.[82] The dual responsive swelling behaviour has also been utilized to reversibly alter the wettability of surfaces.[83] For example, a copolymer of dimethylacrylamide containing azobenzene moieties has been grafted to silicon surfaces, resulting in static contact angle changes of 30° with increasing temperature.[84] Additionally, the azobenzene moieties allowed a shift of LCST by 4 °C upon UV irradiation, which again resulted in a change in contact angle.

Block copolymers

Block copolymers that consist of a poly(*N*-isopropylacrylamide)-*block*-poly{6-[4-(4-methylphenyl-azo) phenoxy]hexylacrylate} (PNIPAM-*b*-PAzoM) have been synthesized using the RAFT polymerization.[85] Here, the photo-control was taken one step further and the self-assembly behaviour of the amphiphilic block copolymer into giant micro-vesicles was investigated. Optical microscopy studies revealed the fusion and deformation of the vesicles upon irradiation.

Various water-soluble diblock copolymers of 2-(dimethylamino)ethyl methacrylate and azobenzene methylacrylate or azobenzene acrylate have been synthesized by Ravi *et al.*[86] They investigated the LCST behaviour with regard to the photoisomerisation of the chromophores. Even though, the obtained shifts of the LCST were only insignificant, they could observe the formation of core–shell micelles.

Another synthetic example of thermo- and light-responsive diblock copolymers was described by Kakuchi and coworkers who combined ATRP and click chemistry.[87] An azide terminated PNIPAM was conjugated to an alkyne-terminated poly(6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate), resulting in a diblock copolymer consisting of thermo-responsive block and one light-responsive block. They found an increase in LCST up to 4.1 °C for a block copolymer containing 1.4 mol% of azobenzene.

A suitable application for temperature- and light-responsive polymers was demonstrated by Perrin and coworkers.[88] They used an azobenzene-modified polyacrylate as an amphiphilic photoresponsive polymer to form a stimuli-responsive emulsion of *n*-dodecane as the oil phase, 0.3 M $NaNO_3$ solution as an aqueous phase and tetraethylene glycol monododecyl ether as a surfactant molecule. The mixture of the surfactant/polymeric emulsifier exhibited a high-sensitivity towards light and temperature and the foaming behaviour could be controlled by applying both stimuli separately (see Fig. 5).

The research on block copolymers has recently been focused on amphiphilic materials that are capable of forming dual responsive micelles. As an example, Yu and coworkers[89]

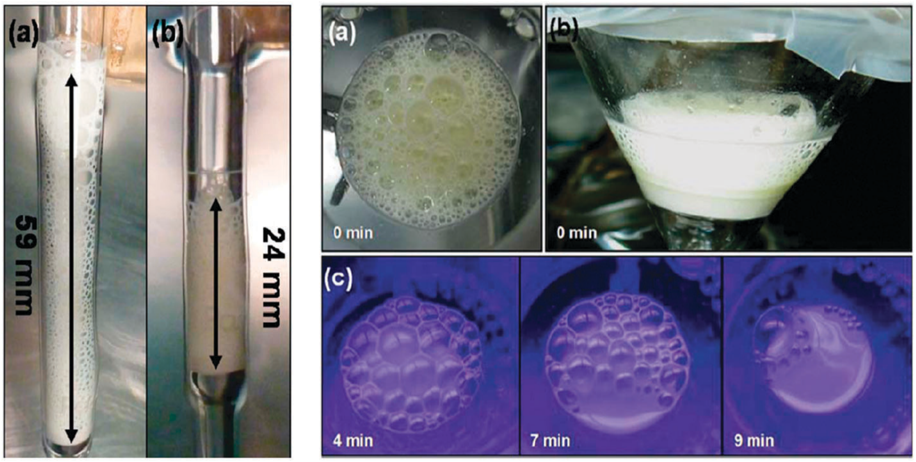


Fig. 5 Left pictures: the pictures show the foaming behaviour of emulsions at temperatures (a) below (T = 18 °C, height: 59 mm) and (b) above (T = 26.7 °C, height = 24 mm), the so-called phase inversion temperature. Right pictures: the pictures of the direct emulsion foams at T = 26 °C before irradiation from the top (a) and from the side. The pictures (c) were taken after UV-light exposure (365 nm) of 4 minutes, 7 minutes, and 9 minutes, indicating that light is a convenient stimulus to control emulsion foam stability. Reproduced from ref. 88 with permission from the Royal Society of Chemistry (RSC).

synthesized diblock copolymers composed of a permanent hydrophilic poly(ethylene oxide) block and a hydrophobic stimuli-responsive block consisting of azobenzene-containing methacrylate and NIPAM in a ratio of 1 : 1 (mol : mol). The size of the formed micellar structures could be changed by increasing the temperature, as measured by dynamic light scattering. However, neither a temperature- nor a light-controlled complete disruption could be observed in the present study.

This motivated the study of similar amphiphilic block copolymers consisting of a hydrophilic poly(ethylene oxide) block and a dual-responsive block having statistically arranged azobenzene and NIPAM groups.[90] It is important to point out here that the responsive block PEO-*b*-PNIPAM had a different ratio between azobenzene and NIPAM comparable to the work of Yu and coworkers. NMR measurements confirmed that only 5 mol% of the azobenzene chromophore had been incorporated. This incorporation ratio was crucial in guaranteeing the photocontrol of the phase transition of the temperature-responsive block. Consequently, the thermo-responsive formation and deformation of micelles as well as a subsequent light-induced isothermal disruption of the same aggregate had been achieved (see Fig. 6). Although, this effect could only be observed in a narrow temperature window in the range around the LCST of the responsive block, these results have highlighted the potential to control aggregation of temperature- and light-responsive block copolymers by applying both stimuli independently.

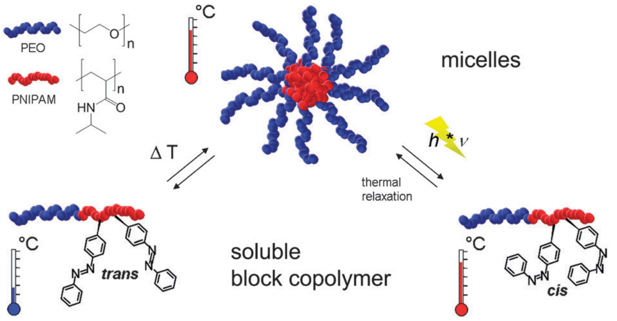


Fig. 6 Temperature and light-controlled formation/disruption of micelles derived from PEO-*b*-PNIPAM block copolymers having azobenzene moieties in the thermo-responsive segment. Adapted from ref. 90 with permission from the Royal Society of Chemistry (RSC).

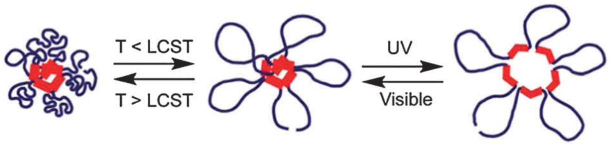


Fig. 7 Schematic illustration of the photo- and thermo-responsive behaviours of the flower micelle. A reversible swelling–deswelling as well as a collapse/reformation of the aggregates could be induced applying either light or temperature as stimuli, respectively. Adapted from ref. 91 with permission from the Royal Society of Chemistry (RSC).

Very recently, Zhao and coworkers described the synthesis of a hydrophobic modified PNIPAM polymer that consisted of short azobenzene segments repeatedly inserted within the main chain.[91] The LCST of the multiblock copolymer was, however, only slightly affected by the *trans* to *cis* photo-isomerisation of the photochromic moieties. The formation of flower micelles in cold water was found and proven by DLS and TEM measurements. These aggregates could be addressed independently by temperature and light as stimuli. The core of the micelles could be stimulated by swelling or deswelling, using alternating irradiation with UV and visible light, respectively. On the other hand, the micelles could be collapsed by changing the temperature according to the hydration/dehydration transition of the temperature-responsive PNIPAM corona (see Fig. 7).

Combination with other stimuli

Research on the temperature- and light-responsive polymers using azobenzene chromophores was extended to additional stimuli such as pH changes.[92] Triply-responsive copolymers on the basis of PNIPAM containing azobenzene moieties were described by Liu and coworkers.[93] They prepared copolymer hydrogels that respond to temperature, light and pH. An interesting example for the combination of different stimuli to tune the cloud points has been demonstrated by Yin and coworkers.[94] For this purpose, a series of hyperbranched poly(ether amine) (hPEA) containing azobenzene moieties was synthesized. The obtained polymer nanoparticles exhibited a sharp stimuli response to temperature, pH, ionic strength and light in a range from 25 to 100 °C. The cloud points in aqueous solution decreased with the increase in azobenzene content, pH value and ionic strength. Furthermore, a light-controlled change in the cloud points as well as in the corresponding nanoparticle size was observed.

Recently, the group of Theato demonstrated another interesting example for applying three different stimuli.[95] They took advantage of the redox reactions of 2,2,6,6-tetramethyl-1-oxyl-piperidine (TEMPO) as side groups as well as the photo-isomerization of azobenzene side groups along the polymer backbone were combined to control the phase separation temperature of a PNIPAM copolymer. Similar dual responsive behaviour of PNIPAM with incorporated TEMPO moieties had been described by Bergbreiter.[96] The LCST behaviour was investigated by means of the cloud points of the triple responsive polymers using turbidity measurements. By adding ascorbic acid into the polymer solution, the cloud points could be increased due to the reduction of the TEMPO moieties. The conversion from the oxyl- into the more hydrophilic hydroxylamine group resulted in an improved hydrophilic interaction with water, which caused higher cloud points. Oxidation of the hydroxylamine-TEMPO moiety back to the radical was achieved by addition of red potassium ferricyanide. As a consequence, a significant decrease in the cloud point temperature could be observed demonstrating that the redox stimulus could be completely reversed. Furthermore, irradiation with UV light (365 nm) resulted in a small but significant increase in the phase transition temperature by 0.3 °C due to the photo-isomerization of the pendant azobenzene moieties from *trans* to *cis*. In analogy to the redox reactions, the photo-isomerization could be reversed by irradiation with visible light. Consequently, the evaluation of these multi-responsive systems for molecular information processing could be demonstrated in the context of logic gates (see Fig. 8).

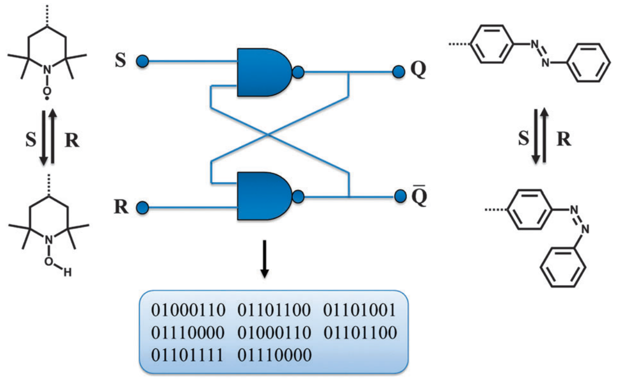


Fig. 8 Evaluation of a multi-responsive PNIPAM polymer having TEMPO and azobenzene moieties for molecular information. Adapted from ref. 95 with permission from the Royal Society of Chemistry (RSC).

Thermoresponsive polymers containing various (non-azobenzene) photochromic functionalities

Statistical copolymers

Although most temperature-responsive polymers use azobenzene as light-responsive functionality, several other examples with different photochromic dyes, photo-cleavable units or photo-cross linking agents in combination with LCST polymers have been reported.

In 2009, the synthesis of temperature- and light-responsive polymers using salicylideneaniline as photochromic units had been described.[97] The copolymers were synthesized *via* a double polymer analogous reaction forming *in situ* salicylideneaniline side group chromophores within PNIPAM copolymers. Indeed, salicylideneaniline has been known to exhibit photochromism both in its crystalline and in its solution phases, with the photo-irradiation process of salicylideneaniline being based on a *keto–enol* tautomerism.[98] All copolymers featured a LCST in aqueous solution, which was dependent on the amount of incorporated chromophoric salicylideneaniline groups and the isomerization state of salicylideneaniline, respectively. Higher values for the cloud points could be measured after UV-light irradiation. However, in all cases, the increase in the cloud points was irreversible. It was assumed that this phenomenon might be due to the stabilization of the excited salicylideneaniline in a polar environment such as water or irreversible cleavage or the decomposition of the chromophore into a more polar counterpart. However, when immobilized on a surface, the use of salicylideneaniline chromophores allowed a photo-control of the wettability of modified surfaces, such as glass, steel or polycarbonate.[99]

Another example for the incorporation of photochromic units into temperature-responsive polymers made use of a fulgimide chromophore and the cloud point dependency of the irradiated chromophore within a PNIPAM copolymer was investigated.[100] The class of fulgimides is well-known to show photochromic behaviour in solution,[101] and consequently, an isomerisation between the *E* and *Z* conformation can usually be observed, as well as a photocycle reaction, depending on the excitation wavelength. Although, the photochromic fulgimide units within the PNIPAM copolymer system showed a light-responsive behaviour, the phase separation temperature was hardly affected by the photo-isomerisation process.

Besides the mentioned fulgimides and salicylideneaniline chromophores, the photochromism of spiropyran within a temperature-responsive polymer received respective attention. The spiropyran moiety adopts the colourless spiropyran form in the dark or under visible light, whereas it can spontaneously be converted into the coloured merocyanine isomer upon irradiation with UV-light.[101] Similar to other photochromic groups, the photo-isomerization process is accompanied by a strong polarity change in a molecule. While the closed spiro-form of the spiropyran is non-polar, the open merocyanine form has a highly polar and electron-rich zwitterionic structure. For this reason, spiropyran has been recognized as a suitable alternative chromophore to the most commonly used azobenzene within temperature- and light-responsive materials.

A prime example for the combination of temperature-responsive PNIPAM and the spiropyran chromophore was reported by Ivanov *et al.*[102] In their study, a PNIPAM copolymer containing 1.9 mol% spiropyran units was synthesized from the corresponding monomers by a free radical polymerization. The copolymer showed a cloud point in aqueous solution in the range between 30 and 50 °C. UV-illumination caused photo-isomerization of the spiropyran units into the coloured merocyanine isomer. Interestingly, the cloud point of the irradiated polymer did not increase, as a more polymer structure would indicate, but decreased after the irradiation. Furthermore, the re-isomerization process of the spiropyran took more than 20 days. Obviously, the open zwitterionic merocyanine form was stabilized in a polar environment such as water.

The same stabilization effect of the open-form by water molecules had been reported by Suzuki and coworkers in 2004.[103] They used a PNIPAM copolymer with spiropyran units for the photo complexation of Pb^{2+} in aqueous solution.

Other groups investigated the swelling behaviour of photo-responsive PNIPAM films containing spiropyran moieties using the quartz crystal microbalance technique. They found that at certain temperatures, the adsorption of water and changes in the viscoelasticity were induced when the corresponding copolymer layer was irradiated by UV-light.[104] PNIPAM hydrogels containing spiropyran groups have previously been studied by Sumaru *et al.*[105,106] They found a volume shrinkage of the gel as well as a proton dissociation under UV-light irradiation. Furthermore, the authors developed a hydrogel membrane and could successfully demonstrate the photo-control of the membrane with regard to the permeation for liquids such as 1 mM HCl solution.

In fact, similar PNIPAM copolymers containing spiropyran groups have been proposed to be used as a thermometer, because of the linear and reversible bathochromic/hypsochromic shift of the absorption spectrum within a wide temperature range while being irradiated (see Fig. 9).[107] The heat-induced bathochromic shift could be explained by the formation of a less polar domain by polymer aggregation when the polymer changed from a coiled to a globular structure at the LCST. Very recently, similar copolymers have been proposed for the selective fluorometric detection of cyanide anions in water at certain temperatures.[108]

In another study, the wettability of copolymer films of PNIPAM possessing spiropyran moieties has been the focus of investigations. The light-controlled wettability change due to the photo-isomerization of the photochromic moieties was analysed by contact angle measurements.[109] When the polymer was applied to a nanostructured surface, contact angle changes from 5° to 123° were observed.

A particular example of a PNIPAM nanogel with spironaphthoxazine (instead of the most commonly used spiropyran) and a pyran-based fluorescent dye has been reported by Son and coworkers.[110] The random copolymer was synthesized by copolymerization and displayed a LCST as well as photochromic behaviour in solution and in the hydrogel state. A temperature dependent fluorescence intensity was observed and the fluorescence of the gel could be modulated reversibly by alternating irradiation with UV and visible light.

Another promising example for a photochromic PNIPAM hydrogel with spironaphthoxazine has previously been proposed by Kim and coworkers for optical data storage.[111,112] Erasable and rewritable photoimaging of the temperature- and light-responsive hydrogel was successfully demonstrated by the authors (see Fig. 10).

Another example for PNIPAM hydrogels containing spironaphthoxazine moieties has been published by Neckers and coworkers.[113] Temperature changes as well as the irradiation with alternating light caused hydrogels to absorb more water. The gel could be swollen by UV-irradiation and deswollen by heating.

In 2008, Irie and coworkers demonstrated in a fascinating study that amphiphilic photochromic diarylethene derivatives having hexa(ethylene glycol) side chains exhibit also thermo-responsive properties.[114] The thermal-induced clouding of these systems could be photo-controlled by alternating irradiation with visible light and UV-light. A large difference of 22 °C was found between the LCST of the open-isomer and the closed-isomer of the diarylethene hybrid system.

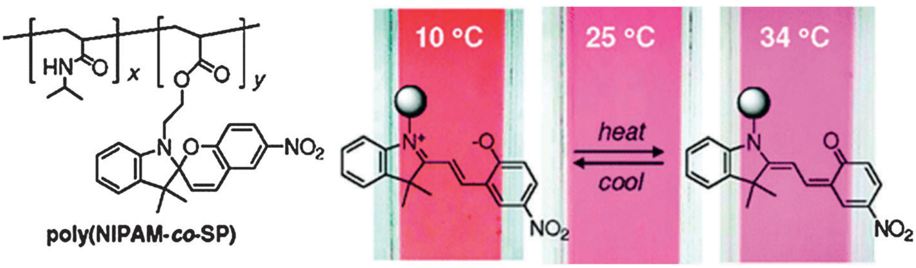


Fig. 9 A simple copolymer, poly(NIPAM-*co*-SP), consisting of *N*-isopropylacrylamide and spiropyran units, could behave as a colorimetric thermometer exhibiting a temperature-responsive linear and reversible bathochromic/hypsochromic shift in the absorption spectra under UV irradiation. Adapted from ref. 107 with permission from the American Chemical Society (ACS).

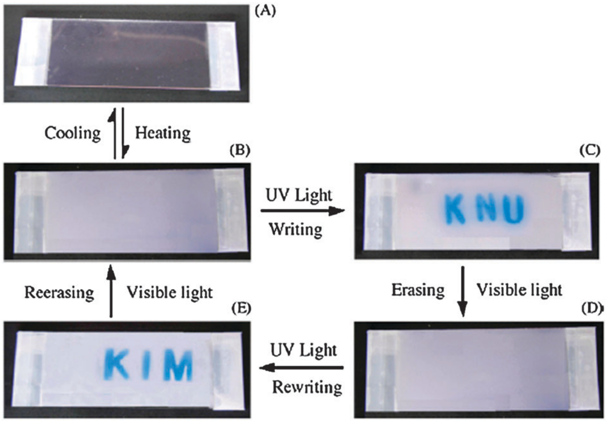


Fig. 10 Use of PNIPAM hydrogel with spironaphthoxazine for optical data storage. Applying heating and cooling, the hydrogel between two glass slides could be switched from sol (a) to gel (b) state, whereas alternating UV and visible light through a mask enabled a writing (c), erasing (d) and rewriting process (e). Reproduced in part from ref. 112 with permission from Elsevier.

The field of temperature- and light-responsive polymers having spiropyran as photochromic units has recently also been extended to multi-responsive systems. A certain approach has been reported combining solvatochromic-, pH-, temperature- and light-responsive behaviour.[115] In this report, copolymers were prepared by the copolymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with the photochromic monomer 1′,3′,3′-trimethyl-6-methacryloyloxyspiro(2*H*-1-benzopyran-2,2′-indoline) (SP). These copolymers exhibited a ''reverse photochromism'' that stabilized the planar zwitterionic form of the chromophore, leading to ''negative solvatochromism'' upon increasing the polarity of the solvent. In addition, it was reported that the PDMAEMA-*co*-PSP copolymers exhibited a reversible pH-responsive character in aqueous media. The addition of strong acids caused the isomerization of spiropyran into the open merocyanine species. The LCST of the copolymers was increased by the content of hydrophilic merocyanine moieties, while the photo-induced isomerization of merocyanine into spiropyran significantly decreased the LCST (see Fig. 11).

Triple-responsive polymers containing spiropyran moieties have also been reported by Garcia *et al.*[116] Here, PNIPAM-allylamine microgels with spiropyran groups were synthesized. The smart gels exhibited photo-, thermal and pH-responsive properties as studied by various dynamic light scattering measurements.

Block copolymers

Double-responsive ''schizophrenic'' block copolymers using spiropyran (SPMA) and di(ethylene glycol) methyl ether methacrylate (DEGMMA) monomers have been reported by Ji and coworkers.[117] It was possible to selectively address each block segment of PSPMA-*b*-PDEGMMA by applying temperature and light as stimuli. At 15 °C and under visible light, the block copolymer was forming core–shell micelles with a diameter of 80 nm with the light-responsive spiropyran block segment as a core and the hydrophilic di(ethylene glycol)methyl ether methacrylate repeating units as a corona. By photo-irradiation with UV-light, the micelles could be disrupted isothermally as the light-responsive block changed the polarity from non-polar (spiropyran) to polar (merocyanine). The average hydrodynamic diameter was decreased to 7 nm, indicating that the block copolymer was molecularly dissolved in water at 15 °C under UV-light exposure. This isothermal light-responsive disruption was fully reversible. After an additional UV-irradiation, followed by a heating step, the formation of inverse micelles with a hydrodynamic diameter of 24 nm could be realized. In this case, the thermo-responsive collapsed DEGMMA polymer formed the core, whereas the polar light-responsive block exhibiting now the merocyanine isomer guaranteed the stabilization of the formed nanoparticles (see Fig. 12). Accordingly, this study represents again a fascinating contribution to applying light and temperature independently in order to control the morphology of nanoaggregates in solution.

Another interesting example has been reported by Liu and coworkers.[118] They have synthesized a PNIPAM block copolymer P(NIPAM-*co*-NBDAE)-*b*-P(NIPAM-*co*-SPMA) brush containing spiropyran groups as photo-switchable acceptors and benzoxadiazoles as donors for fluorescence resonance energy transfer

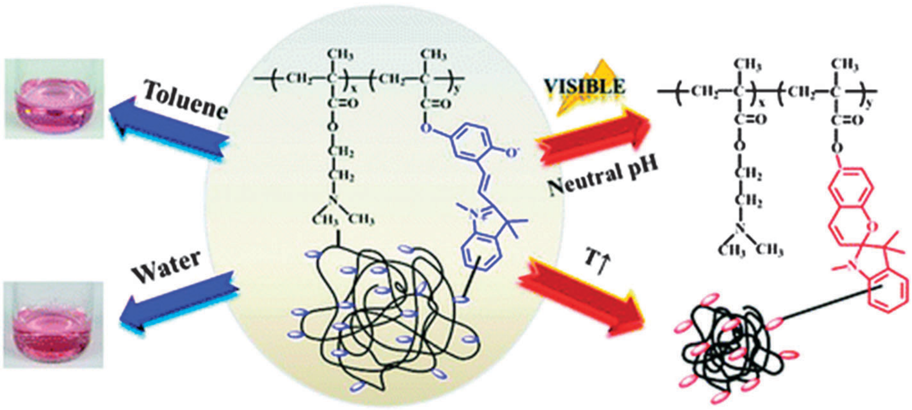


Fig. 11 Schematic illustration of overall stimuli (solvent, light, temperature and pH) that could be applied within PDMAEMA-*co*-PSP copolymers. Adapted from ref. 115 with permission from the American Chemical Society (ACS).

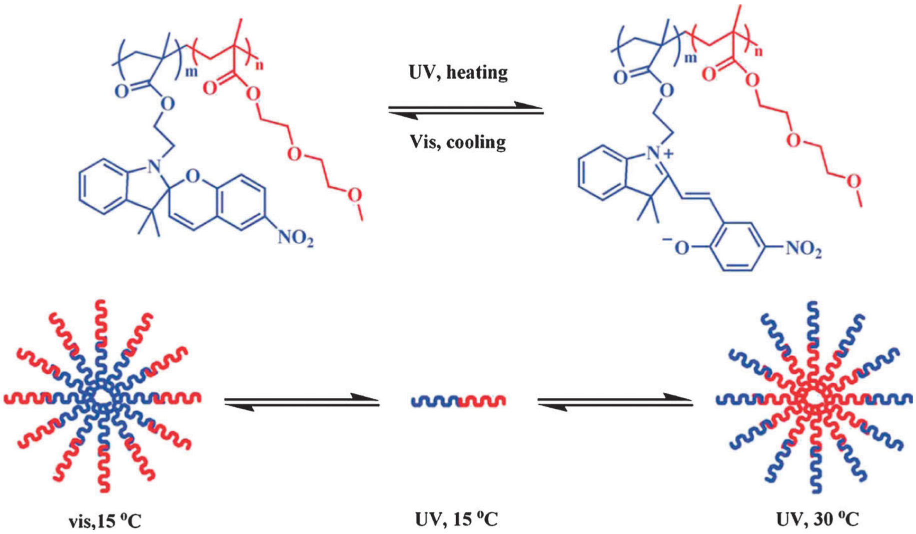


Fig. 12 Schematic representation of double-responsive micellization of ''schizophrenic'' PSPMA-*b*-PDEGMMA in aqueous solution. Depending on temperature and light, the block copolymer formed micellar structures with various segments as core and corona, respectively. Adapted from ref. 117 with permission from John Wiley and Sons.

(FRET) on silica nanoparticles. The block copolymer brushes exhibited a collapse within a broad temperature range. As a consequence, the local distance between both dyes could be changed in aqueous dispersion. The fluorescence emission of the spiropyran could enable the FRET process between both dyes, which could be switched by temperature due to the changes in the distance between the donor and the acceptor through swelling/deswelling (see Fig. 13).

The group of Zhao described the synthesis of doubly photo-responsive block copolymers using either azobenzene- or spiropyran-containing poly(*N*,*N*-dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM) and poly[methoxy-di(ethylene glycol)methacrylate] (PDEGMMA).[119] Turbidimetry measurements and NMR analyses were performed to investigate phase transition behaviours in aqueous solution before and after simultaneous photo-reactions of the two blocks, respectively. The LCST of the block copolymers could be fine-tuned by the photo-isomerization of the photochromic groups and hence this study highlights nicely the potential of complex photoreaction to control the solution properties of thermo-responsive polymers.

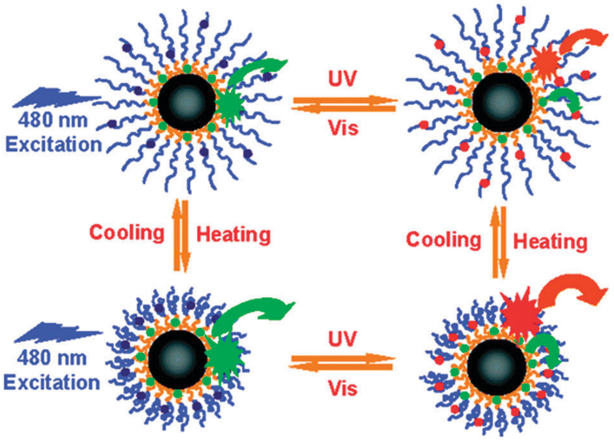


Fig. 13 Schematic illustration of the reversible modulation of a multicolor fluorescent system fabricated from hybrid silica nanoparticles coated with thermo-responsive P(NIPAM-*co*-NBDAE)-*b*-P(NIPAM-*co*-SPMA) brushes. The FRET process within the functionalized nanoparticles could be switched on or off *via* UV or visible light irradiation. In addition, the FRET efficiency could be tuned *via* thermo-induced collapse/swelling of responsive polymer brushes. Adapted from ref. 118 with permission from the American Chemical Society (ACS).

Thermo-responsive polymers containing photocleavable functionalities

Recently, polymers with photocleavable groups received a similar attention to those having photochromic moieties. These systems have been proposed for micellization and dissociation transitions. In one particular study, the thermo- and light-sensitive hydrophilic block copolymer poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene glycol) acrylate-*co*-*o*-nitrobenzyl acrylate) was synthesized and the micellization/dissociation transitions in water in response to temperature changes and UV-irradiation were further investigated.[120] The corresponding block copolymer was synthesized starting from a PEO macro initiator using the ATRP technique (see Fig. 14). At low temperatures, the block copolymer was molecularly dissolved in water. At higher temperatures above the LCST of poly(ethoxytri(ethylene glycol))-acrylate, a self-assembly into polymeric micelles with the thermo-responsive block building the micelle core and the PEO block forming the corona was observed by dynamic light scattering. Upon UV-irradiation, the *o*-nitrobenzyl group was cleaved and the LCST of the thermo-responsive block increased by 12 °C. Consequently, the dissociation of the micelles into unimers was observed. A further increase in the temperature induced the reformation of micelles again (see Fig. 14).

The same research group has further investigated dually responsive aqueous gels having *o*-nitrobenzyl groups.[121] For this study, linear triblock ABA copolymers composed of

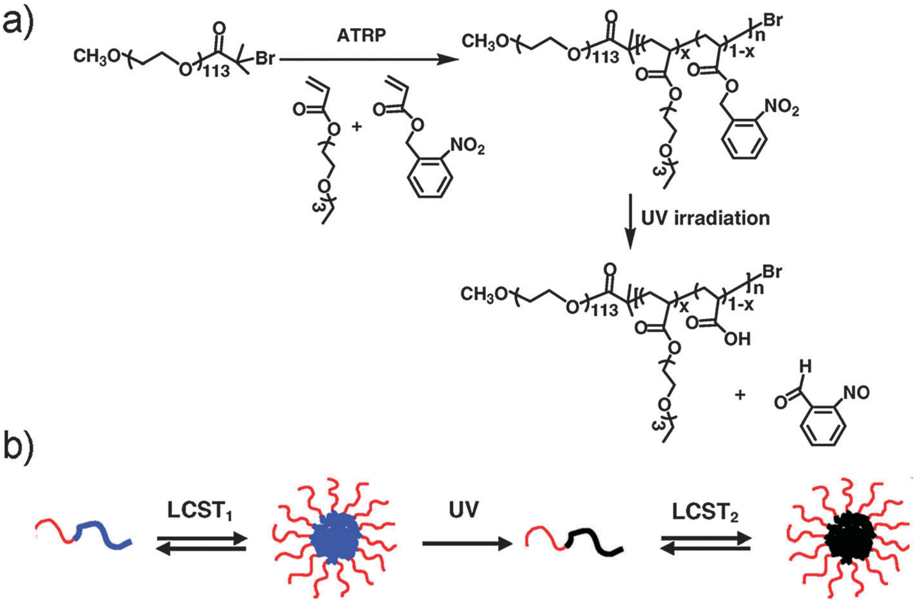


Fig. 14 (a) Synthetic procedure of thermo- and light-responsive poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene glycol)acrylate-*co*-*o*-nitrobenzyl acrylate) through ATRP followed by the photocleavable reaction through UV-irradiation. (b) Multiple micellization and dissociation transitions of poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene glycol) acrylate-*co*-*o*-nitrobenzyl acrylate) in response to temperature changes and UV-light irradiation. Reproduced from ref. 120 with permission from the American Chemical Society (ACS).

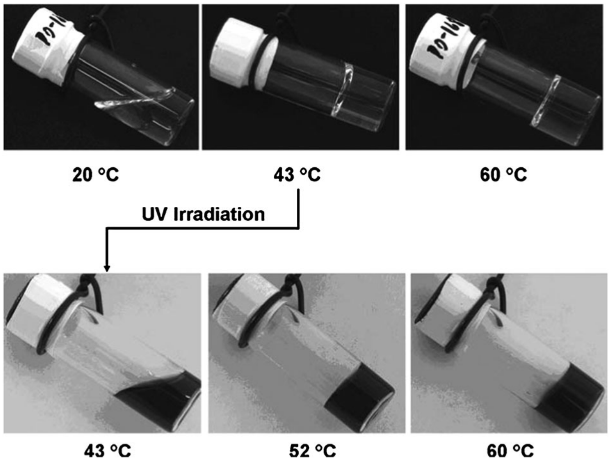


Fig. 15 Optical pictures of 10 wt% solutions in water of the ABA triblock copolymers at various temperatures. The pictures (upper row) show the transition of the polymer solution from sol (20 °C) to gel (43 °C) applying heat as stimulus. At a constant temperature of 43 °C, UV irradiation of the gel was applied which triggered the reverse transition from gel to sol. The sol which was irradiated at a temperature of 43 °C (lower row) underwent again temperature-induced sol-to-gel transition which, however, took place at a higher temperature (52 °C). Adapted from ref. 121 with permission from the Royal Society of Chemistry (RSC).

poly(ethoxytri(ethylene glycol))acrylate with photocleavable groups and poly(ethylene oxide) as a middle segment have been synthesized by ATRP. In aqueous solution, the triblock copolymer showed a thermo-induced reversible sol–gel transition and a UV-triggered gel-to-sol transition at a constant temperature as well. The UV-irradiated solution could undergo a subsequent temperature-induced sol–gel transition, which took place at a higher temperature (see Fig. 15). Similar studies of temperature- and light-induced sol-to-gel transitions of diblock copolymers have previously been investigated by the same group.[122]

Liu and coworkers prepared dually responsive microgels.[123] They prepared microgels *via* free radical emulsion polymerization of *N*-isopropylacrylamide, 5-(2′-(dimethylamino)ethoxy)-2-nitrobenzyl acrylate and acrylates containing FRET donor and acceptor dyes (nitro-benzoxadiazole and rhodamine B, respectively). UV irradiation above LCST, *i.e.* collapsed microgel, resulted in a photocleavage and formation of acrylic acid moieties, which lead to a re-swelling of the microgel as monitored by FRET.

Ionov *et al.* described the reversible phase-transition of PNIPAM based copolymers in conjunction with photocleavable moieties (poly(*N*-isopropylacrylamide-*co*-2-nitrobenzylacrylate)).[124] They have shown that upon UV irradiation and respective photocleavage of *ortho*-nitrobenzyl esters the resulting poly(*N*-isopropylacrylamide-*co*-acrylic acid) featured a higher LCST. Consequently, they could utilize films of the dual-responsive copolymer as smart photoresists in a photolithographic patterning. Another example for thin films consisting of LCST-systems featuring photocleavable groups as light-responsive functionality was proposed by Lai *et al.*[125] They grafted light-responsive PNIPAM polymers comprising *o*-nitrobenzyl groups on the outer surface of mesoporous silica nanoparticles. A light-controlled release of encapsulated biological molecules was demonstrated.

Wang and coworkers presented an alternative approach towards photoresponsive copolymers, based on a Wolff-rearrangement of 2-diazo-1,2-naphthoquinone (DNQ).[126] In a post-polymerization modification approach, they attached 2-diazo-1,2-naphthoquinone-5-sulfonyl chloride onto poly(*N*-isopropylacrylamide-*co*-*N*-hydroxymethylacrylamide). The resulting copolymer was responsive to three different stimuli (light, pH and temperature).

Thermo-responsive polymers containing cross-linkable functionalities

In fact, besides photocleavable or photochromic groups, cross-linkable functionalities represent the third big light-responsive functionality to tune the properties within thermo-responsive materials by light. Here, the cross-linking process can be either reversible or irreversible, depending on the incoming light and the cross-linking reagent.

As one example, thermo-responsive nanogels from photo-cross-linkable copolymers of NIPAM and 2-dimethylmaleinimido ethylacrylamide have been reported by Kuckling *et al.*[127] In this process, colloidal nanogels could be formed by UV-irradiation from aqueous solutions of the thermo-responsive polymers. The size of the obtained nanogels could be controlled by the concentration of the polymer in solution, the amount of incorporated chromophores in the polymer chains and the emulsifier concentration.

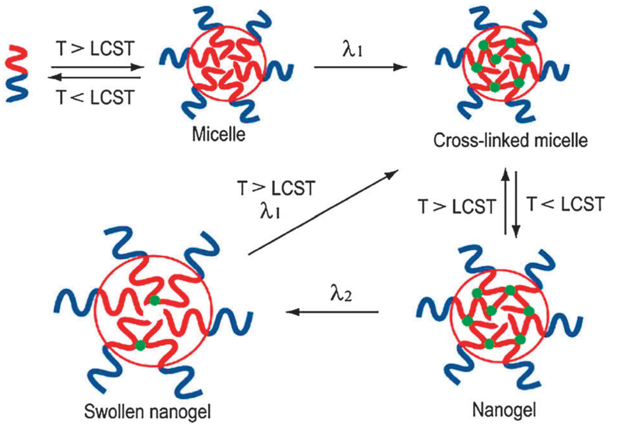


Fig. 16 Schematic concept of the preparation and the photo-controlled volume change of the nanogel. Reproduced from ref. 128 with permission from the American Chemical Society (ACS).

Thermo-responsive nanogels based on photo-controllable cross-linking reactions of coumarin have successfully been proposed and demonstrated by Zhao and coworkers.[128,129] In these studies, temperature- and light-induced size changes of nano aggregates and networks could be realized. They synthesized diblock copolymers composed of poly(ethylene oxide) and poly[2-(2-methoxyethoxy) ethyl methacrylate-*co*-4-methyl-[7-(methacryloyl)oxyethyloxy]coumarin] (PEO-*b*-P(MEOMA-*co*-CMA)). The smart nanogels could be obtained by photo-cross-linking of the micellar aggregates at temperatures below the LCST of the P(MEOMA-*co*-CMA) block through dimerization of coumarin side groups at a wavelength higher than 310 nm. Under $\lambda < 260$ nm, the reverse photocleavage of the network was observed, which resulted, consequently, in a reduction of the cross-linking density followed by a swelling of the nanogel (see Fig. 16).

Furthermore, Zhao and coworkers could describe in another study the synthesis of corona-cross-linked temperature-responsive polymer vesicles with coumarin as a reversible cross-linking agent.[130] These polymer vesicles showed large reversible and rapid volume transitions in aqueous solution in response to temperature change.

As an extension of their previous studies, Zhao and coworkers explored the photo-tunable LCST of poly(*N*,*N*-dimethylaminoethyl methacrylate) [PDMAEMA] containing coumarin moieties.[131] The copolymers were obtained by copolymerization of the monomers (see Fig. 17).

The LCST could be fine-tuned by means of UV-light irradiation, which caused intrachain cross-linking reactions within

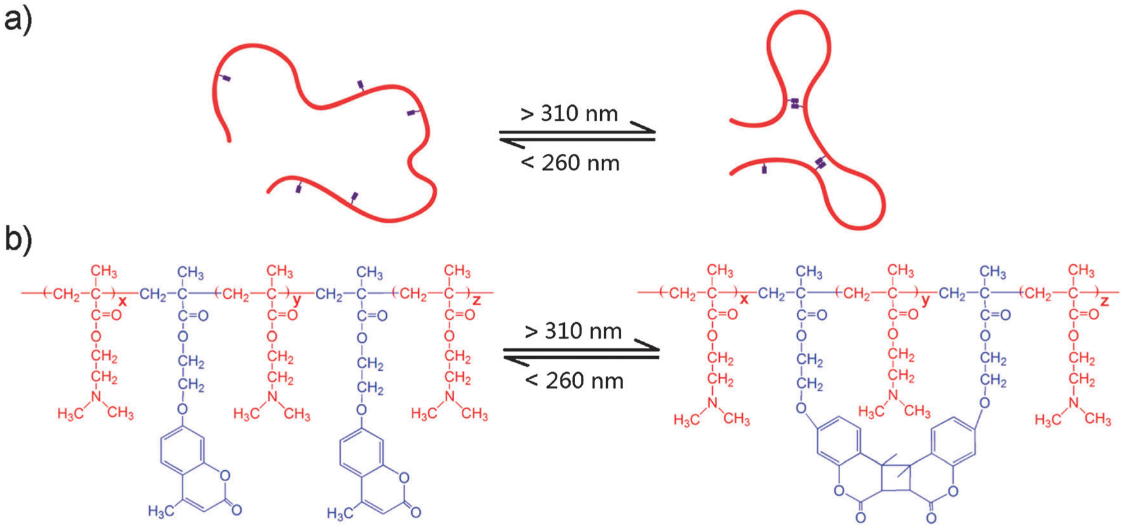


Fig. 17 (a) Schematic illustration of the formation of cross-linked thermo-responsive poly(*N*,*N*-dimethylaminoethyl methacrylate) loops through intrachain photo-dimerization of coumarin group moieties. (b) Chemical structure of a statistical copolymer based on poly(*N*,*N*-dimethylaminoethyl methacrylate) having photo-cross-linkable coumarin side groups. Adapted from ref. 131 with permission from the American Chemical Society (ACS).

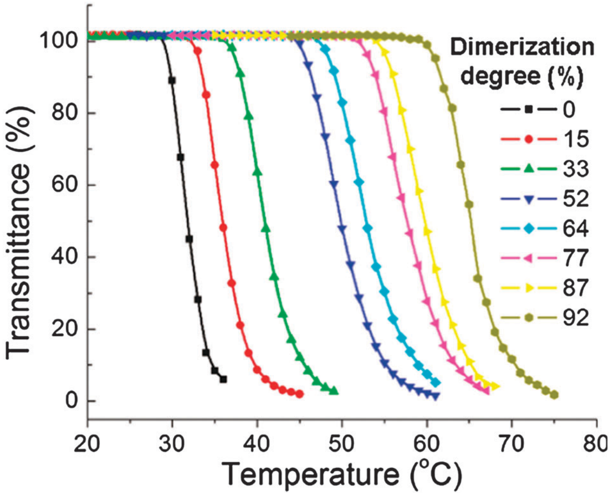


Fig. 18 Transmittance change as a function of temperature for PDMAEMA containing coumarin moieties solutions with samples photo-dimerized to different degrees demonstrating a sequentially fine-tuning of the LCST by light-irradiation. Reproduced from ref. 131 with permission from the American Chemical Society (ACS).

the temperature-responsive polymer. The photo-dimerization resulted in LCST shifts up to 30 °C higher for the full dimerization of PDMAEMA having 8 mol% coumarin functionalities incorporated as measured by turbidimetry (see Fig. 18). These findings were explained by a topical effect of the cross-linked polymer.

Conclusion and outlook

Temperature- and light-responsive polymers combining both stimuli have been known for almost 30 years. Indeed, the first report in the late 1980s aimed at the photo-control of the LCST of PNIPAM having azobenzene moieties. In this paper, we were able to present many examples and applications to this effect that have been published by several research groups over the decades. For the fine-tuning of the LCST using light as stimuli, several thermo-responsive polymers using photochromic, photo-cleavable or photo-crosslinking functionalities have been proposed and investigated. These systems have also been extended to other stimuli, such as pH or redox-reactions yielding multi-responsive systems. As a highlight, several block copolymers have been designed that allow for the temperature- and/or light-controlled self-assembly into polymeric micelles. A thermal and light-controlled formation and deformation of nanoaggregates was demonstrated in several examples, applying both stimuli individually. Some potential applications such as in thermometers, nanosensors, optical data recording, controlled drug release, controlling foams or even in molecular computing have been proposed and demonstrated. It is worth pointing out here that more than 75 percent of all given examples in the context of temperature- and light-responsive polymers have been published within the last five years. This emphasizes the importance of stimuli-responsive materials combining light and temperature in polymer chemistry in recent days. Furthermore, the huge number of stimuli-responsive polymers combining light and temperature can be regarded as a success of modern polymer synthesis methods. Controlled radical polymerization techniques enabled a very precise control over the polymerization process. Defined end-groups as well as complex molecular architectures of stimuli-responsive polymers have been realized through these new synthetic tools. Furthermore, post-polymerization modification chemistries have been demonstrated to be a powerful tool to synthesize polymers that were otherwise difficult to achieve.

Although many developments have already been presented, there is still a demand in academia to continue the investigations of such stimuli-responsive materials in the future. Finally, potential applications for these systems in our daily life should be devised and further developed. Here, many unfinished tasks are still ahead, such as their use as stimuli-responsive nanocarriers, a general rapid responsiveness of the applied stimuli and the exact reproducibility, which represent a challenge and need yet to be solved. Although it is very difficult to foresee a suitable trend or even a ''market'' for temperature- and light-responsive systems in the near future, we hope that this systematic review will be an inspiration for scientists in academia and industry to further proceed and intensify research on these materials and their applications in the future.

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