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Smart microcapsules based on photo-isomerizable moieties

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1 Introduction

Environmentally responsive materials have been the subject of great interest in the last two decades due to their versatile applications. Such materials are sometimes called "smart" because their properties allow them to react in a specific way to external stimuli, such as temperature, pH, light, ionic strength and magnetic fields. The previous chapter of this book was dedicated to an overview of different types of photo-stimuli materials that have been used for light-triggered release of encapsulated actives. In this chapter we focus on photosensitive microcapsules, whose shells are based on azobenzene moieties. It is well known that aromatic azobenzenes are excellent candidates as molecular switches because they can exist in two forms: namely the *cis* (*Z*) and *trans (E)* isomers, which can interconvert both photochemically and thermally. This transformation induces a molecular movement and a significant geometric change; therefore the azobenzene units are excellent candidates to build dynamic molecular devices. This strategy is very attractive in microencapsulation technology, because it allows control over the conformation and consequently the release of the encapsulated active, such as drugs, perfume, etc., not only in required time but also in a reversible way without the addition of any reagent or different stimuli. According to results presented in literature and patents, development and testing of photo-control release microcapsules has had a significant impact on:

1. environmentally friendly production methods:
   - encapsulation and smart controlled release of crop protection agents (CPAs), i.e. pesticides;
2. health protection:
   - encapsulation and smart release of protective substances (i.e. used as a main component of sun protection creams) only at the appropriate time – during sun light illumination – in order to minimize their side-effects;
   - encapsulation and smart release of pharmaceutics or supplements in order to protect their properties from the external environmental;
   - encapsulation and smart release of pharmaceutics or supplements in order to mask their taste;
   - increase of standard of life while decreasing the costs;
   - encapsulation and smart release of different active agents with future potential applications in electronics, textiles, catalysis, graphics and printing, the chemical industry, etc.

This chapter is divided into two parts. In the first part we discuss the photoisomerization processes of azobenzene molecules while in the second part we describe selected examples of microcapsules whose shells are formed by materials containing these UV-sensitive moieties in their structures.

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2 Photoisomerization of azobenzene

Azobenzenes are organic molecules that have two aromatic rings linked by an azo group (N=N). They have properties that have led to some applications of great importance, mainly for the chemical industry. The azobenzenes are highly colored compounds and belong to the group of so-called FD&C (food, drug and cosmetics) dyes. Azobenzene was described for the first time in 1834 [1], and in 1937 – one century later – G.S. Hartley published a study on the influence of light on the configuration of N=N double bonds [2]. The exposure of a solution of azobenzene in acetone to light allowed the discovery of the *cis* isomer. This was the starting point of the development of one of the best organic molecular switches described so far. Nowadays, azobenzene dyes represent approximately 60% of the world production of industrial dyes [3]. Like a C=C double bond, azobenzenes have two geometric isomers (*Z*/*E*) around the N=N double bond, the *trans*-isomer (*E*) is ~12 kcal/mol more stable than the *cis* isomer (*Z*) [4]. The energy barrier of the photoexcited state is ~23 kcal/mol, such that the *trans*-isomer is predominant in the dark at room temperature [5].

The *trans*-azobenzene easily isomerizes to the *cis* isomer by irradiation of the *trans*-isomer with a wavelength between 320 and 350 nm. The reaction is reversible and the *trans*-isomer is recovered when the *cis* isomer is irradiated with light of 400–450 nm, or heated. For many azobenzenes, the two photochemical conversions occur on the scale of picoseconds, while the thermal relaxation of the *cis* isomer to the *trans*-isomer is much slower (milliseconds to days). The photo-induced isomerization of the azobenzenes leads to a remarkable change in their physical properties, such as molecular geometry, dipole moment or absorption spectrum [6, 7]. The isomerization process involves a decrease in the distance between the two carbon atoms in position four of the aromatic rings of azobenzene, from 9.0 Å in the *transform* to 5.5 Å in the *cis* form (Figure 1) [8]. The *trans*-azobenzene is almost flat and has no dipole moment, whereas the *cis* isomer presents an angular geometry and a dipole moment of 3.0 D. One of the rings rotates to avoid steric repulsions caused by the facing of one of the π clouds of one aromatic ring to the other. The free volume requirement is that the *cis* is larger than the *trans*, with estimates of approximately 0.12 nm^3 required for isomerization to proceed via an inversion of the azo bond, and 0.28 nm^3 for a rotation about the azo bond [9]. The UV-vis absorption spectrum of azobenzene presents two characteristic absorption bands corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions. The transition $\pi \rightarrow \pi^*$ is usually in the near UV region and is common to carbonate systems, such as stilbene [10]. The electronic transition $n \rightarrow \pi^*$ is usually located in the visible region and is due to the presence of lone electron pairs of nitrogen atoms [11]. Due to this second electronic transition, the dynamic photoisomerization process of azobenzenes is different to the carbonate compounds [12]. Azobenzene undergoes *trans-cis* isomerization by $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitations and *cis-trans*-isomerization by exciting into the S_1 or S_2 state. The sum of the quantum yields is different to unity, which indicates multiple pathways for isomerization [9].

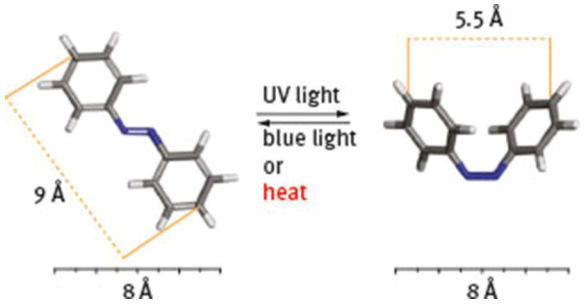

Figure 1: Azobenzene photoisomerization. The *trans* form (left) can be converted to the *cis* form (right) using an appropriate wavelength (UV at 300–350 nm) of light. A different wavelength (visible blue light >400 nm) can be used to convert the molecule back to the *trans* form. Alternately, the molecule will thermally relax to the stable *trans* form.

The aromatic azocompounds are classified into three types based on the order of their energetic electronic states $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ [5]. This order depends on the electronic nature of the aromatic rings of azobenzene. Each type of azobenzene also has a predominant color defined by the wavelength of the maximum absorption band (λ_{max}) (indicated in brackets in each case):

- Azobenzene type: the $\pi \rightarrow \pi^*$ band is very intense in the UV region and there is one $n \rightarrow \pi^*$ weaker in the visible region (yellow color). The electronic nature of the aromatic rings is very similar to simple azobenzene (Ph–N=N–Ph).
- Aminoazobenzene type (*o*- or *p*-(X)–C_6H_4–N=N-Ar): the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands are very close or collapsing in the UV-vis region. In this case, the azocompounds have electron-donor substituents (X) in the *ortho* or *para* positions (orange color).

– Pseudo-stilbene type [(X)–C_6H_4–N=N–C_6H_4–(Y)]: the absorption band corresponding with $\pi \rightarrow \pi^*$ transition is shifted to red, changing the appearance order with respect to the band $n \rightarrow \pi^*$. The azocompounds of this type present donor substituents (X) and electron acceptors (Y) at the 4 and 4′ positions, respectively (push/pull system) (red color).

The isomerization process normally involves a color change to more intense colors. The absorption spectra of both isomers differ mainly in the following aspects (see Figure 2) [13]:

– *Trans*-isomer: the absorption band $\pi \rightarrow \pi^*$ is very intense, with a molar extinction coefficient (ε) ~ 2–3 × 10^4 $M^{-1} \cdot cm^{-1}$. The second band ($n \rightarrow \pi^*$) is much weaker ($\varepsilon \sim 400\ M^{-1} \cdot cm^{-1}$) as this transition is not allowed in the *trans-isomer* by symmetry rules.

– *Cis* isomer: the absorption band $\pi \rightarrow \pi^*$ is shifted to shorter wavelengths (hypsochromic effect) decreasing significantly in intensity ($\varepsilon \sim 7–10 \times 10^3\ M^{-1} \cdot cm^{-1}$). The electronic transition $\pi \rightarrow \pi^*$ (380–520 nm) is allowed in the *cis* isomer, resulting in an increase in the intensity ($\varepsilon \sim 1500\ M^{-1} \cdot cm^{-1}$) with respect to the *trans*-isomer.

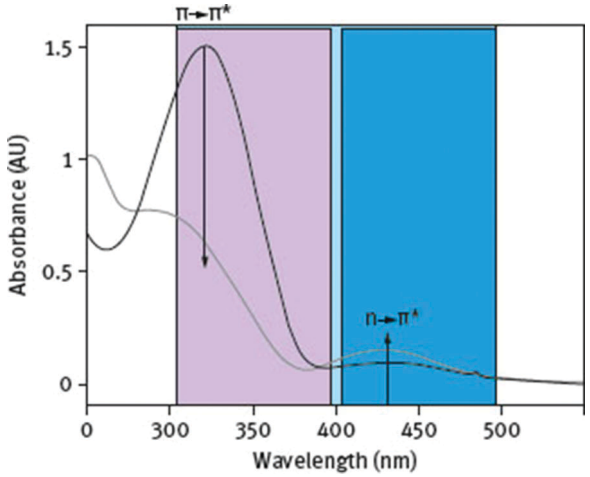

Figure 2: Respective example of a UV spectrum of azobenzene compounds.

These differences allow a photochemical interconversion by irradiation with light of a certain wavelength, obtaining different proportions of the *cis* and *trans*-photostationary states. The excitation caused by the wavelength is dependent on the nature of the substituents of the aryl groups. In most cases, *trans* → *cis* isomerization is promoted by irradiation with wavelengths between 320 and 380 nm, while exposures to $\lambda \sim 400–450$ nm favor the *cis* → *trans*-photoreversion. The mechanism is not well established. Several mechanistic studies have been performed on the isomerization reversal route *cis* → *trans* of azobenzene to investigate the effect of the substituents on the benzene rings as well as the influence of several parameters. The available data suggest that the isomerization of azocompounds can proceed through the reversal of one of the N–C bonds or by the rotation of the N=N bond. The non-bonding electron pair of each nitrogen atom may lead to one $n \rightarrow \pi^*$ electronic transition ($S_0 \rightarrow S_1$) with inversion at the nitrogen atom (inversion mechanism). Conversely, the isomerization can also occur through a rotation mechanism, which involves a $\pi \rightarrow \pi^*$ transition ($S_0 \rightarrow S_2$) (Figure 3) [9, 14, 15].

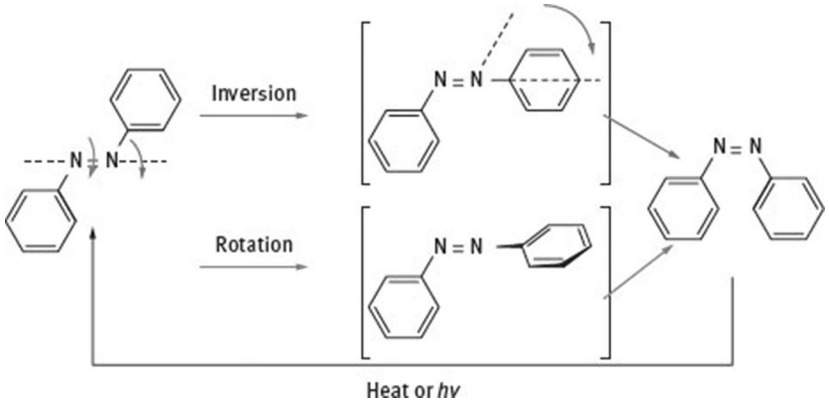

Figure 3: Mechanistic proposals for the isomerization of azobenzenes.

3 UV-sensitive microcapsules based on azobenzene moieties

Using the isomerization of azobenzene and its derivatives to modulate the structure of delivery systems, and thus to trigger the light-induced release of various compounds, has been reported in the literature. Different methods and concepts have been used for microcapsules preparation.

3.1 Liposome microcapsules

The first study of incorporating azobenzene moieties in a photoresponsive system to affect release was published by Kano et al. in 1980 [16]. The authors incorporated an amphiphilic azobenzene moiety along with dipalmitoylphosphatidylcholine (DPPC) at various molar ratios and were able to modulate the release profiles of liposomes based on the azo moiety of choice, the composition of photostationary state, and the degree of incorporation in the liposome. The authors characterized the photoisomerization process using a UV spectroscopy by illuminating the *trans*-azo compound at 366 nm for 10 s. The *trans*-compound formed a photostationary state with 80% *cis* isomer, which reverts back to *trans*-when irradiated at > 420 nm. The authors also studied the resulting osmotic shrinkage of the vesicles upon incorporation of azo compound by measuring the optical density of the solutions. They encapsulated bromothymol, a blue dye, in the lipid bilayer of liposomes formulated from DPPC and subsequently showed that the permeation of the dye into water increased with greater incorporation of the *cis* azobenzene moiety (formed by irradiation). Unfortunately, in these pioneering studies, percent release and duration of release upon pulsing were not entirely characterized.

Since this seminal study there have been numerous publications utilizing this concept. Many systems developed since have incorporated azobenzenes in lipid backbones and formulated liposomes that are photoresponsive [17–19].

The photo-responsiveness of the liposomes arises from the fact that in the *transconfiguration* the molecules pack tightly in the bilayer. When irradiated with UV light, they undergo *trans-cis* isomerization, which leads to distortions in the packing of the bilayer and causes the liposomes to become "leaky", allowing the encapsulated drugs to be released. Irradiation of azobenzene results in the formation of a photostationary state and the composition of this state determines the release rate of the drug. More recently, Smith et al. have used phototriggerable liposomes to trigger gelation of an alginate solution by releasing calcium chloride upon irradiation with 385 nm light for 1 min. Such on-demand gelation is important in tissue engineering applications [20].

The photoisomerization concept has also been successfully utilized in the preparation of photoresponsive micelles. These systems take advantage of the change in net dipole moment upon switching from the *trans*-orientation (no net dipole moment) to the *cis* orientation. This leads to disruption in the hydrophobic-hydrophilic balance of the self-assembled micelles and causes reorganization and subsequent release of encapsulated contents [20].

3.2 Self-assembly microcapsules

Self-assembly of amphiphilic block copolymers induces the formation of nanosized polymeric microcapsules or micelles, which have been widely explored as carriers for enzymes or non-biological catalysts as well as containers for drug or gene delivery. As amphiphilicity is the principal basis of such self-assembly, some approaches have been developed to modulate the polymeric assemblies for controlled drug delivery through tuning the amphiphilicity of the block copolymers. Generally, the drug species encapsulated in or attached to the polymeric assemblies can be released via reversible or irreversible disassembly of the hydrophobic core-forming segments. However, the self-assembly of amphiphilic block copolymers usually involves the use of organic solvents and suffers from complicated preparation processes. More than a decade ago Kataoka's group [21] developed a method for preparing block copolymer assemblies on the basis of electrostatic interactions. This new family of polymeric assemblies is formed by double-hydrophilic block copolymers, containing ionic and nonionic water-soluble segments (block ionomers), and can incorporate many charged polymers, including synthetic polyions, enzymes, DNA, RNA, and others [22]. One great advantage of this approach is that such assemblies are formed in water, and no organic solvent is required for their preparation. Moreover, the block ionomers with appropriate molecular weight and composition can also form micelle-like or vesiclelike aggregates. The basic mechanism of the formation of such polymeric assemblies involves the core precipitation of the charged blocks of block ionomers with the oppositely charged polyions. Besides the block ionomer-polyion systems, Kabanov et al. [23] proposed a simple method to prepare block ionomer complexes by electrostatic complexation of block ionomers with oppositely charged surfactants. Such a block ionomer complex can be depicted as an amphiphilic supramolecular block copolymer, in which the nonionic block functions as the hy-

drophilic part while the electrostatic complex of the ionic block and aggregated surfactant counterions serves as the hydrophobic part. It is known that by introducing stimuli-responsive moieties such as azobenzene onto the surfactants, the surfactant aggregates can be tuned towards controllable disassembly.

Wang et al. [22] for the first time demonstrated the possibility of controlled self-assembly and disassembly of the block ionomer and surfactant microcapsules through tuning the amphiphilicity of the surfactants. The authors fabricated the UV-responsive microcapsules through an electrostatic association between an azo-containing surfactant and a double-hydrophilic block ionomer, poly- (ethylene glycol)-b-poly(acrylic acid) (PEG43-PAA153), as it is shown in Figure 4. They found that loading and release of fluorescent molecules included in the microcapsules could be achieved by reversible self-assembly and disassembly under UV light irradiation. By introducing stimuli-responsive surfactants into the block ionomer microcapsules complex, one may broaden the application of this new class of supramolecular materials. Such novel materials containing azobenzene moieties in their structures are of both basic and practical significance, especially as prospective nanocontainers for drug delivery.

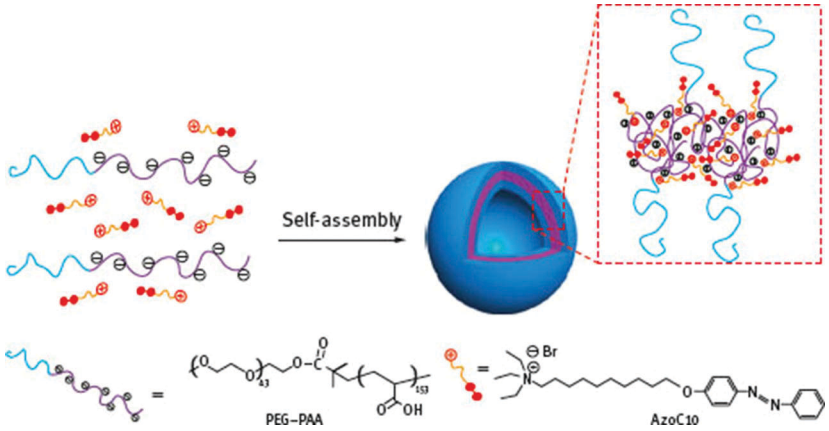

Figure 4: Schematic illustration of the self-assembly of the block ionomer microcapsules. Reprinted with permission from [22].

3.3 Layer-by-layer microcapsules

As shown in this book, numerous strategies have been used to develop microcapsules with different functionalities. One of the simple but functional methods is the so-called layer-by-layer (LbL) assembly technique. By using the electrostatic interactions between oppositely charged polyelectrolytes, the LbL approach offers diversified multilayer capsule systems with controllable architectures and properties. Moreover, the stepwise polymer deposition procedure facilitates the functionalization of the capsule formations; a typical example is cargo substance encapsulation [24]. Polyelectrolytes are basic components for LbL capsule fabrication. Diverse polyelectrolytes have been used to build up capsules. Different combinations of the oppositely charged polyelectrolytes with active functional groups endow their capsules with unique properties, which would affect their further applications.

In an early example, Möhwald and co-workers reported that layer-by-layer (LbL) capsules containing an azo dye in their shell allowed photochemical control of the permeability of the shell [25]. In this study, the microcapsule shell was composed of an azo dye – Congo red (CR) – and different polymers, including poly(styrenesulfonate, sodium salt) (PSS), poly- (allylamine hydrochloride) (PAH), and poly(diallyldimethylammonium chloride) (PDDA). Figure 5 shows the general procedure of LbL self-assembly of PDDA/CR onto the (PSS/PAH)3/PSS shells templated on MF latex particles.

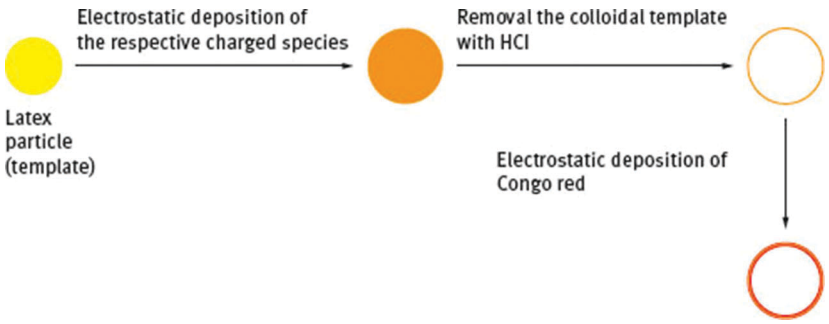

Figure 5: General procedures for the fabrication of hollow capsules composed of CR and polyelectrolytes [25].

In order to observe morphology change of the microcapsules shell before and after irradiation, the authors used scanning force microscopy (SFM). Moreover, the optical changes of the capsules were verified by using confocal laser scanning microscopy and SFM. All results obtained by authors provide useful insights into the photochemical reaction mechanisms on the self-assembled PDDA/CR composite capsules and release of encapsulated material. This kind of capsule with photocontrolled permeability could be of particular interest for applications in drug delivery, photocatalysis, optical materials, and related medical areas such as photodynamic therapy or skin care.

Bédard et al. [11] also constructed the microcapsules containing azobenzene moieties through LbL self-assembly of sodium salt of azobenzene, poly(vinylsulfonate) and poly(allyamine hydrochloride); however, contrary to Möhwald and co-workers, they investigated how *trans-cis* isomerization of the azo moieties influences the permeability changes of the shell and on encapsulation of the active material instead of its release during light irradiation. According to the authors, incorporation of azobenzene groups can cause shrinking of the microcapsules wall, increase their permeability and as a consequence encapsulate required materials.

More recent examples using stimuli-responsive capsules based on azobenzene moieties in the capsule wall comprise the work of Yi and Sukhorukov [24, 26], Lin et al. [27], or Xiao et al. [28].

Yi and Sukhorukov fabricated UV-responsive microcapsules containing azobenzene by sequential deposition of oppositely charged poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and poly(diallyldimethyl ammonium) chloride (PDADMAC). The authors showed that the combination of PDADMAC and PAZO led to aggregation of PAZO segments in the progress of polymer deposition, which facilitated the large extent of J aggregates when the capsules were exposed to UV light. Moreover the same authors [26] developed a multifunctional capsule system using an electrostatic attraction LbL assembly, which can integrate both encapsulation and release processes in one system, simply triggered by only one external stimulus. Dual-functional complex microcapsules (PDADMAC/PAZO-)4-(DAR/Nafion)$_2$ containing both diazonium and aozbenzene groups were proposed to realize a time-dependent UV response for successive encapsulation and release. Upon exposure to UV light, the DAR/Nafion layers underwent a rapid *in situ* crosslinking and hence sealed the capsule shells through diazonium-related photolysis. Then, further gradual shell swelling was followed by realignment of azobenzene molecules in PDADMAC/PAZO layers, as it is shown in Figure 6. Fluorescent polymers were consequently investigated as cargo substances. Results indicated that continuous UV light-triggered rapid cargo encapsulation over a time scale of minutes and gradual release with continuous irradiation over hours. Morphological changes of the capsules shell during UV irradiation were investigated by SEM and are reported in Figure 7.

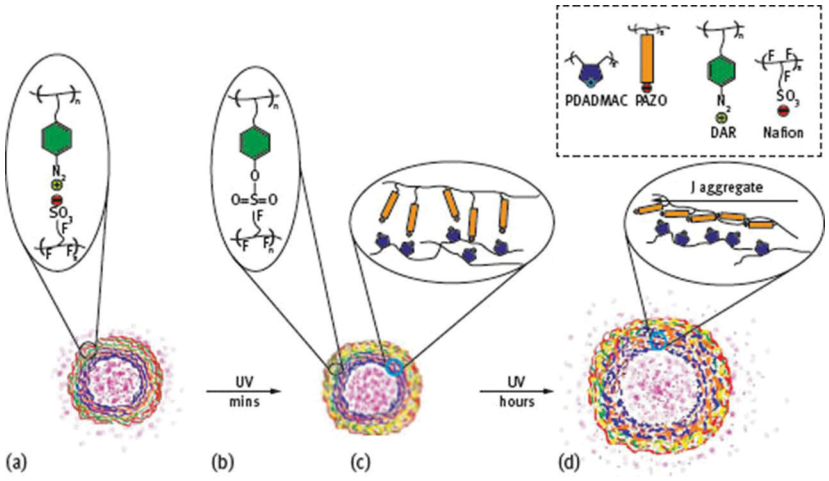

Figure 6: Schematic illustration of UV-induced complex capsule shell sealing and further swelling. Reprinted with permission from [26].

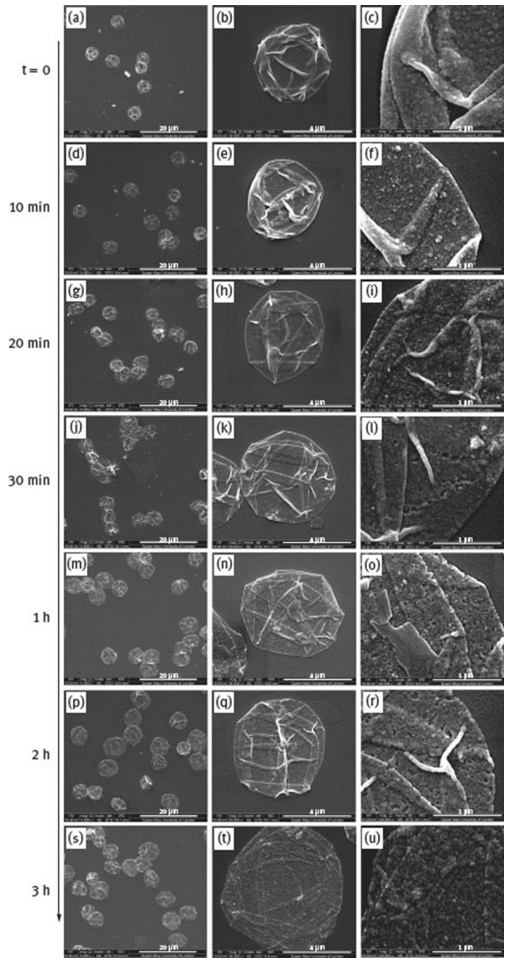

Figure 7: Scanning electron microscope (SEM) images of complex microcapsules before (first row) and after UV irradiation of 10 min (second row), 20 min (third row), 30 min (fourth row), 1 h (fifth row), 2 h (sixth row), and 3 h (last row) at different magnifications. Reprinted with permission from [26].

It is well known that the driving force for the LbL assembly of microcapsules mainly uses electrostatic attraction; however, this limits the building blocks to a narrow range of oppositely charged and water-soluble polymers.

Contrary to Yi and Sukhorukov or Möhwald and co-workers, both Xiao et al. and Lin et al. designed photoswitchable LbL capsules that use a supramolecular interaction as the driving force of LbL assembling and layer drug loading. The capsules were assembled by host polymeric layers containing α-CD and guest polymeric layers containing azo. Using the supramolecular interaction instead of electrostatic interaction as the driving force of LbL the authors have been able to enhance the stability of microcapsules in various pH conditions. Xiao et al. investigated UV-sensitive microcapsules based on host–guest interactions between carboxymethyl dextran-graft-α-CD (CMD-g-α-CD) and poly(acrylic acid) Naminododecane p-azobenzeneaminosuc-cinic acid (PAA-C12-azo) which were assembled LbL on $CaCO_3$ particles. They used an antineoplastic drug modified with α-CD α-CD-rhodamine B (α-CD-RhB) as a model drug, which was loaded onto PAA-C12-azo layers by host–guest interaction. After removal of $CaCO_3$ particles by ethylenediaminetetraacetic acid (EDTA), hollow microcapsules loaded with α-CD-RhB were obtained. Because the interactions between α-CD and azo were photosensitive, obtained capsules were dissociated upon irradiation by a UV lamp (λ = 365 nm) due to the transformation of *trans*-azo to *cis*-azo (see Figure 8). As a result, more than 60% of the drug was released from the microcapsules within 300 min of irradiation (Figure 9), while in a dark environment, the drug release was very slow and less than 5% of the drug was released in 300 min.

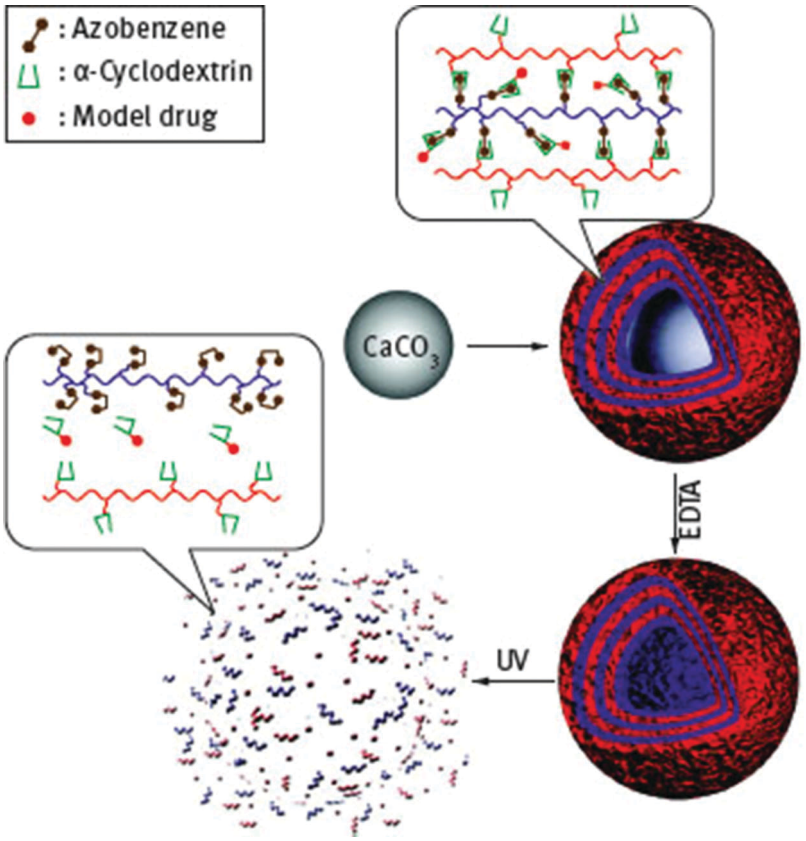

Figure 8: LbL microcapsules prepared by Xiao et al. Reprinted with permission from [28].

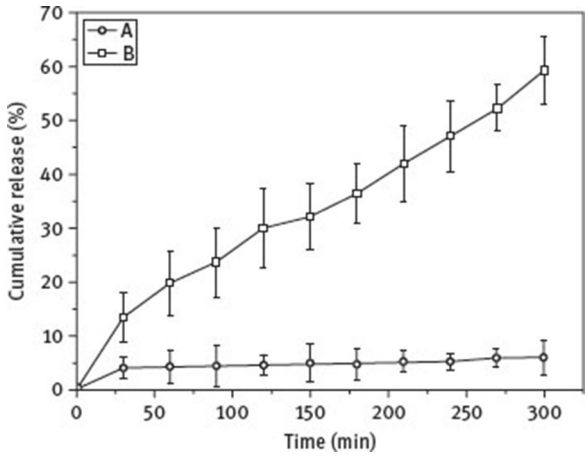

Figure 9: Drug release behaviors of $(PAA\text{-}C_{12}\text{-}azo)_5/(CMD\text{-}g\text{-}\alpha\text{-}CD\&\alpha\text{-}CD\text{-}RhB)_5$ microcapsules in the dark (A) and under 365 nm UV light irradiation (B). Reprinted with permission from [28].

Using a similar method, Lin and co-workers designed microcapsules; however, these were much more "advanced" compared to those prepared by Xiao and co-workers. In this investigation the host–guest interactions were based not only between β-cyclodextrin (β-CD), and azobenzene (like in Xiao's study) but also between β-CD and adamantane (AD). Prepared microcapsules were able to be controllably switched between the "on" and "off" state. In this study Lin et al. showed that the stable host– guest interactions between β-CD and AD maintained the structure as a permanent frame, while the reversible UV-sensitive ones between azo and β-CD could form a denser membrane to keep the drug inside. In order to prepare this type of microcapsules, authors used two specific polymer chains: poly(acrylic acid-graft-azobenzene-graft-adamantane) (PAA-g-AD-g-azo) and poly(aspartic acidgraft-b-cyclodextrin) (PASP-g-β-CD). Poly(ethylene glycol)5000-graft-fluorescein isothiocyanate (PEG5000-FTIC) was loaded inside the microcapsules as a model drug. In the "off" state, trans-azo participates in the host-guest interaction with β-CD, and the model drug cannot pass. When the UV ray switches azobenzene moieties to the cis-state, the interaction between azobenzene and β-CD diminishes. The electrostatic repulsion between the negatively charged polyelectrolyte chains makes the membrane no longer dense enough to keep the model drug inside. As the photoisomerization of azobenzene moiety is reversible,

the release process could be controlled by UV irradiation reversibly. Once the "on" state microcapsule is stimulated by visible light, it would switch back to the "off" state, i.e. the release could be ceased and recommenced controllably. These photosensitive microcapsules exhibit great potential in biomedical applications.

3.4 Interfacial polymerization microcapsules

To date, self-assembly techniques have been mainly used in the fabrication of microcapsules containing azobenzene units; however, the self-assembled microcapsules are generally not robust. Therefore, the stable, reversible photoresponsive microcapsules are highly desirable but little reported to the best of our knowledge. Tylkowski et al. [29] prepared new lightly crosslinked liquid crystalline polyamide microcapsules that contained azobenzene moieties in the main chain, by using an interfacial polymerization method. The preparation procedures for this technology, also known as interfacial condensation, have been thoroughly described in the literature [30, 31]. Briefly, the microcapsule wall is formed from monomers that are dissolved in the two separate phases (oil and water phase) and they polymerize at the interface of the emulsion droplets. For example, monomers such as diamine can be dissolved in the water and the aqueous phase is dispersed in the oil phase. The second monomer that is oil-soluble, e.g. diacryl chloride, is then added and reacts with the first monomer at the interface forming the wall material. Different types of polymers may be produced by selecting different monomers but most publications refer to polyamide membrane. Tylkowski et al. prepared microcapsules whose shell was constituted by liquid crystalline polyamide and contained either toluene as the core, or concentrated solutions of naphthalene or β-carotene. According to the authors, obtained results were the first published example of microcapsules whose shell is completely constituted by a liquid crystalline lightly crosslinked polymer. They published results concerning the characterization of these microcapsules, which show that release could be easily triggered by irradiating with UV light at 364 nm for a few minutes. This suggested that microcapsules that meet the target of specific applications can be designed by optimizing characteristics such as the state of order of the shell, its range of thermal stability and the structural changes that occur upon irradiation.

Figure 10 shows the release of β-carotene from these polyamide microcapsules in water at 20 °C, in the time range 0–5.5 min, in the absence (▲) and in the presence (▪) of continuous irradiation with UV light, measured as described in the experimental part. The difference between the two curves is straightforward: in the absence of irradiation, release was practically negligible and the plateau value of about 2.5% reached in the first minutes remained constant even after 120 min observation. Differently, when microcapsules were submitted to continuous irradiation with UV light, after an induction period of about 2 min, β-carotene was quickly released and reached its highest concentration value after 5 min. It is important to underline that the initial time corresponds to the UV lamp switch-on; the observed induction time can be therefore reasonably ascribed to the time needed by the polymer for re-arranging in the isotropic structure, as a consequence of photoisomerization. Moreover optical micrograph during the release of β-carotene from these polyamide microcapsules at room temperature after suspending 20 min in water (Figure 11a,b) clearly confirmed the occurrence of release: in the case of the sample suspended in water without irradiation, a trend towards the formation of large agglomerates of β-carotene (dark spots) into the core of microcapsules was observed (Figure 10a). However, when the sample was irradiated microcapsules looked almost empty: moreover, they did not look broken or damaged, thus confirming that β-carotene release was due to a change in the barrier properties of the shell material as a consequence of UV irradiation.

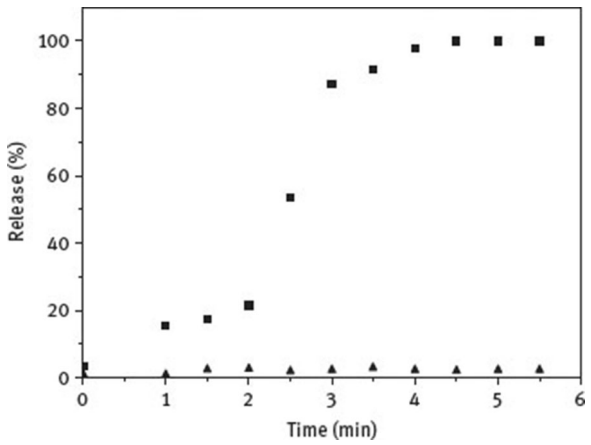

Figure 10: Release kinetics of b-carotene from polyamide microcapsules in water at 20 °C in the absence (▲) and in the presence (▪) of continuous irradiation with UV light. Reprinted with permission from Elsevier [29].

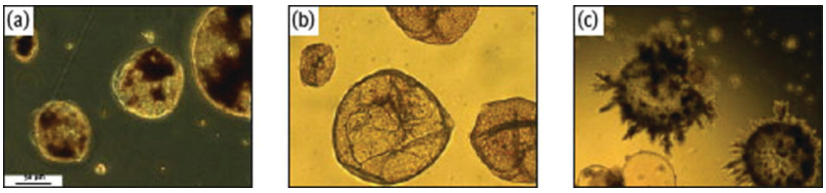

Figure 11: Optical micrographs during the release of β-carotene from the polyamide microcapsules at room temperature after suspending 20 min in: (a) water, (b) water under irradiation with UV light, and (c) tetrahydrofuran. Reprinted with permission from Elsevier [29].

Marturano et al. [32] by using miniemulsion interfacial polymerization synthesizeed nanosized capsules also based on a lightly crosslinked polyamide containing azobenzene moieties in the main chain. The obtained nanocapsules were loaded either with toluene or with the fluorescent probe Coumarin-6 (dissolved in toluene) as a core. Under continuous UV irradiation the polymer underwent *E-Z* photoisomerization allowing the release of the encapsulated material. In this study, variation in diameter of the nanocapsules with the time of UV irradiation was detected through dynamic light scattering (DLS) analysis. Between 10% and 30% growth was observed, depending on the sample.

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