

# Chapter 1

## Introduction and background

### 1.1 Introduction

The nanoscale (from the ancient Greek *νᾶνος*, meaning dwarf) refers to structures with at least one dimension sized from 1 to 100 nm.<sup>[1]</sup> Substances in this size regime can exhibit peculiar properties that are dramatically different from the bulk solids as well as from the individual molecules, such as a lower melting point, a higher conductivity, a greater elasticity or strength, a higher reactivity, catalytic capacities, or a different color.<sup>[2]</sup> As opposed to the typical lustrous color of gold bars, colloidal solutions of spherical gold nanocrystals appear vividly red, owing to the collective oscillation of the confined conduction electrons being in resonance with the incident light.<sup>[3]</sup>

Materials containing nanosized subunits are termed nanomaterials. Their macroscopic properties are governed by the large interface area per unit volume. Over the last several decades, there has been an ever-rising surge of scientific activities on nanomaterials.<sup>[4]</sup> They can be employed in a vast range of applications, for instance in medicine, electronics, optics, biology, catalysis, and energy production,<sup>[5]</sup> and are found more and more in commercial products.<sup>[6]</sup> Major driving forces behind this boost were the emergence and improvement of advanced microscopic techniques and the craving of modern technologies for a rampant miniaturization.<sup>[7]</sup> It is forecast by many that we are on the verge of an era where nanomaterials will reshape our daily life just as steel did in the industrial age.<sup>[8]</sup>

Although synthetic polymers are usually not regarded as nanoscaled objects by themselves, they are ideal and cheap candidates for uniting with inorganic nanoparticles.<sup>[9–11]</sup> The formed organic–inorganic hybrid materials, or nanohybrids, can adopt the best properties of both constituents,<sup>[12]</sup> in exact analogy to the mythological creatures combining body parts of more than one species. Because of the outstanding property combinations, this class of composite materials holds significant promise in a variety of fields. The polymer component can impart long-term

colloidal stabilization, solubility, reduced protein adhesion, or an even dispersion. By synergistic effects, completely new properties can also emerge.<sup>[13]</sup> Of the range of different nanohybrid structures that can be designed, layered nanoparticles with an inorganic core and a polymer shell are typical examples.<sup>[14,15]</sup>

Conversely, the performance of a polymer matrix, regarding process ability, strength, stiffness, wear resistance, appearance, or simply the cost, can be greatly enhanced by capitalizing on the nature and properties of an embedded nanoparticulate filler.<sup>[16–20]</sup> Thanks to their low-price, universality, ubiquity, and their non-toxicity, nanosized silica particles are often used for this task. Natural archetypes for the formed synthetic nanostructured materials with an interstitial organic phase are, for example, bone and nacre.

With a view to potential sensor, actuation, drug-delivery, or catalytic applications, polymers which react to external stimuli with a drastic change in their properties, so-called “smart polymers”, are especially promising candidates for components of multifunctional nanohybrids. By far the most prominent representative of this class is poly(*N*-isopropylacrylamide) (pNIPAm). Its abrupt precipitation from aqueous solutions can be triggered by temperature, additives, and pressure. It is, with this regard, also regarded as a model system for the conformational behavior of proteins.

The precise control of the polymer characteristics is essential for the effective design of nanohybrids with a defined structure.<sup>[21]</sup> For many applications, it is also mandatory to incorporate a functional group into the polymer chains, through which they can be linked covalently to the inorganic substrate, rather than relying on weak polymer physisorption. The synthesis of polymers, which fulfill these conditions, from common industrial monomers has been enabled by the advent of reversible-deactivated radical polymerization (RDRP) techniques in the late nineties. This has meant a huge leap forward in polymer science. By the use of special mediating agents, these techniques allow for the facile large-scale production of macromolecules with defined molar masses and complex architectures. Suitable anchor groups for the grafting of the polymer chains to a surface can be easily introduced as part of the controlling molecules. Alternatively, it is also possible to directly tether the mediating agent to the surface. Polymerizations in the presence of surfaces functionalized in this way usually lead to higher grafting densities. Reversible addition–fragmentation chain transfer (RAFT) polymerization is arguably the most versatile representative of RDRP techniques. It proceeds via a degenerative chain-transfer mechanism which induces an equilibrium between propagating macroradicals and dormant mediating agents carrying dithio moieties, for example trithiocarbonate groups. In addition to the characteristics shared with other important RDRP techniques, the RAFT process inherently possesses three unique

features, which render it particularly promising for employment in the production of sophisticated nanohybrid materials:<sup>[22,23]</sup>

- The RAFT agent can be immobilized on a solid substrate via its stabilizing Z-group, leading to the peculiar mechanistic situation that in surface-confined polymerizations, the polymer chains propagate unattached in the interstitial solution phase. Hence, at the end of the polymerization, no irreversibly terminated polymer chains are linked to the surface.<sup>[24,25]</sup>
- The sulfur-containing mediating RAFT groups themselves are capable of being anchored to gold surfaces. Therefore, after controlling the radical polymerization, they can also fulfill a second purpose.<sup>[26]</sup>
- Polymers carrying multiple RAFT groups along the backbone chain are synthetically accessible with exceptional ease.<sup>[27]</sup> The possibility to form several links to gold can give rise to novel nanostructures.

**The scientific goals of this work** were to exploit these special features and the versatility of the RAFT process for the production of new and advanced nanohybrids containing inorganic particles. As the first step, synthetic pathways to the following suitable components for nanocomposites were intended for exploration:

- Gold nanoparticles of different sizes, which can be easily functionalized with RAFT agents or polymers, either via an accessible and reactive gold surface, or via suitable functional groups on the decorating ligands.
- Specially designed RAFT agents carrying one or more suitable functional anchor groups, with which they can be irreversibly immobilized on nano-sized silica particles of different types or the produced functionalized gold nanoparticles via their Z-group. (The direct coating of gold nanoparticles with RAFT agents is impeded by the fact that all RAFT groups themselves are susceptible to chemisorption on gold.)
- Polymers of *N*-isopropylacrylamide carrying single terminal trithiocarbonate end groups or multiple trithiocarbonate groups evenly distributed along their main chain. Samples varying molar masses and numbers of trithiocarbonate groups were planned to be synthesized to enable comparative experiments.

In a modular way, these building blocks were intended to then be used to produce organic-inorganic nanohybrids, either by carrying forward the principle of surface-confined Z-RAFT polymerization, probing the suitability of the designed RAFT agents on different substrates, or by direct assembly of the different types of polymers

and gold nanocrystals. A special focus was planned for the production of surface-bound polymer nanoloops, which are usually considered especially challenging to generate.

Since the color of colloidal gold crystals depends on the interparticle spacings,<sup>[28]</sup> it was envisaged that the combination with the smart pNIPAm would lead to a material, in which the response to outer stimuli would go along with a change in the color of the nanohybrids.<sup>[29]</sup> For the targeted sensor applications,<sup>[30,31]</sup> the responsive behavior of the pNIPAm component was intended to be analyzed individually under high pressures. Because of the entailed experimental effort, this is an often neglected aspect, which nevertheless does not make it any less important.

In the experiments of grafting polymers to gold nanocrystals, an especially intriguing question was which kind of structures result when polymers with multiple trithiocarbonate anchor groups are employed.

To complete the studies, viable analysis methods to help answer this question and characterize the produced nanohybrids were hoped to be found.

## 1.2 Theoretical background

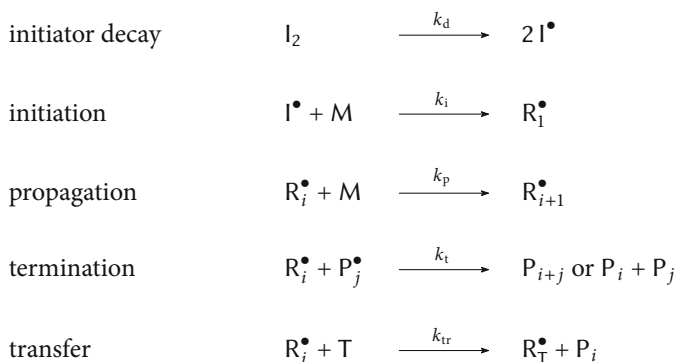
### 1.2.1 Polymers

Polymers consist of macromolecules, in which many self-repeating and covalently linked subunits, called monomers, are incorporated. Natural biopolymers which are produced by living organisms—polynucleotides, polypeptides, and polysaccharides (sugars)—are the basis of life and constitute the majority of organic material on this planet. Since the foundation of modern macromolecular science by the pioneering works of Hermann Staudinger in the beginning of the 20<sup>th</sup> century,<sup>[32]</sup> artificially created synthetic polymers have assumed an ever-increasing role for the modern society and shape the appearance of our civilization. Steady worldwide research has led to the emergence of tailored materials with a huge range of applications, spanning domains such as packaging, clothing, infrastructure, paints, medical equipment, electronics, sports and musical equipment, and the automotive, aircraft, and space industries.<sup>[33]</sup> The polymer properties are mainly directed by the choice of monomer and their topology.<sup>[34]</sup>

#### 1.2.1.1 Radical polymerization

*Radical polymerization* is arguably the most widely used method for the production of synthetic polymers, both in industry and academic laboratories.<sup>[35]</sup> A great variety of vinyl monomers are amenable to this technique, including (meth-)acrylates, styrenes, (meth-)acrylamides, butadiene, and vinyl acetate, and it is generally very tolerant towards most functional groups and a wide range of reaction conditions. Radical polymerization can be performed with very low experimental effort and is therefore in most cases more efficient than other techniques. Since it belongs to the group of *chain-growth polymerizations*, where unsaturated monomer molecules add onto the active site (here the radical function) on a growing polymer chain one at a time, high degrees of polymerization are even achieved at low monomer-to-polymer conversions. (For the other principal polymerization technique, the *step-growth polymerization*, where the monomer molecules first form dimers, which then in turn couple to longer oligomers and eventually to polymers, the mechanism demands a very high extent of reaction and stoichiometry to achieve high molecular weights.)

**Conventional radical polymerization** Scheme 1.1 shows the five elementary reactions of conventional radical polymerization. It is called “conventional” to indicate that no other substances but the basic ingredients which are necessary for



**Scheme 1.1:** Elementary reactions of conventional radical polymerization.  $I$  denotes an initiator fragment,  $M$  a monomer molecule,  $R$  a radical,  $P$  a polymer chain, and  $T$  a radical transfer partner. The chain-lengths are indicated by the indices  $i$  and  $j$ . Hence,  $R_1$  is a monomeric radical, and  $R_{i,j}$  are macroradicals. The variables  $k_d$ ,  $k_i$ ,  $k_p$ ,  $k_{tr}$ , and  $k_t$  denote the rate coefficients of initiator dissociation, initiation, propagation, radical transfer, and termination.

the polymerization are contained in the system. In industry, most radical polymerizations are performed in the conventional way. The first step of the mechanistic scheme is the production of radicals. In most cases, this is achieved by the thermally, chemically, photochemically, or redox-activated decay of initiator molecules. Radicals can also be generated without designated initiator molecules by high-energy radiation, plasma, or the self-initiation of certain monomers (e. g. styrene). The thus produced radical then adds to a monomer molecule and starts the polymerization (initiation). By addition of further monomer molecules to the active chain end, the radical chain continues to grow (propagation) until the radical function is transferred to another species (monomer molecule, polymer chain, solvent, ...), which can in turn continue or re-initiate the polymerization,\* or the radical function is terminated by combination or disproportionation with another radical.<sup>[36]</sup>

Both transfer and termination reactions lead to the production of non-active, so-called *dead* chains, which can no longer participate in the polymerization. The life-time of active chains does not exceed the range of a few seconds and only a very small fraction of polymer chains grow simultaneously.<sup>[37]</sup> For these two reasons, the molar mass and the chemical composition of the polymer material are very difficult

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\* Specifically added agents which form very stable radicals and can therefore bring the polymerization to a stop are called *inhibitors*.

to control and the resulting polymers therefore possess very broad molar-mass distributions ( $\mathcal{D} \geq 1.5$ , see section 1.2.1.2). Furthermore, it is often impossible to incorporate functional groups into the polymer backbone or to produce complex architectures, such as block-, star- or comb-polymers.

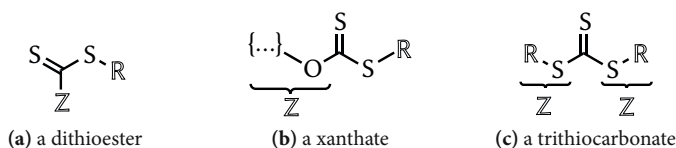
The advantages of conventional radical polymerization lie in its high tolerance towards impurities like water, its high reaction rate and its cost efficiency.

**Reversible-deactivated radical polymerization** In 1956, the term *living polymerization*<sup>[38]</sup> was coined by Szwarc for polymerizations in which the growth of all polymer chains starts simultaneously and neither transfer nor termination reactions take place.<sup>[39,40]</sup> Since this leads to all chains having the same life-time, the resulting molar-mass distribution is very narrow (see section 1.2.1.2) and the average molar mass can be controlled by the stoichiometry of the system or the reaction time. After completion of the polymerization, the active center remains at the macromolecular chain ends and the reaction can be continued with additional monomer molecules. In the case of a different type of monomer, the production of block copolymers is possible.<sup>[41]</sup>

Originally, Szwarc had referred this denomination only to *anionic polymerization*. Over the following years, this concept of living polymerization could be successfully expanded also to *cationic*,<sup>[42]</sup> *coordinative*,<sup>[43]</sup> *ring-opening*,<sup>[44]</sup> and *group-transfer polymerization*.<sup>[45]</sup>

Given the universality, ease, and efficiency of conventional radical polymerization, it goes without saying that it had been a covetable objective in polymer chemistry to find ways of performing a radical polymerization which exhibits living characteristics. But it was only in 1982 that this concept could at least in part be realized, when so-called *iniferters* were intensively examined by Otsu.<sup>[46–48]</sup> Iniferters are compounds which are able to simultaneously act as *initiators* and *transfer* and *terminating* agents in a radical polymerization. Because of slow initiation, these systems still lack control over the obtained average molecular weight as well as the molar-mass distribution.

In the late nineties, polymerization techniques were finally established which could truly combine the versatility of radical polymerization with the control of living polymerization, which were then termed *controlled* (or “*living*”) *radical polymerizations*.<sup>[35,49]</sup> Nowadays, the term *reversible-deactivated radical polymerization* (RDRP) is recommended by the International Union of Pure and Applied Chemistry (IUPAC)<sup>[50]</sup> and should therefore be used preferably.<sup>[51]</sup> The control of these techniques is in general based on one of two major principles which mechanistically govern the polymerization by inducing a dynamic equilibrium between



**Fig. 1.1:** Chemical structures of important types of RAFT agents. Z denotes the stabilizing group, R the re-initiating leaving group. The ellipses express that a fraction of a larger molecule is shown. Note that not all trithiocarbonates are symmetrical and have two leaving groups as shown in c.

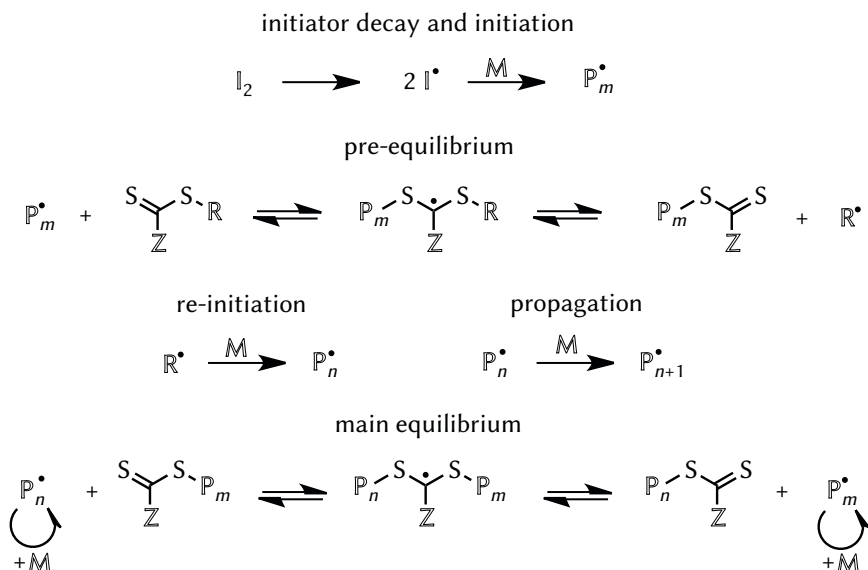
dormant chains and propagating radicals: *reversible termination* or *reversible chain transfer*.

The most important examples of polymerizations based on reversible termination are the *atom transfer radical polymerization (ATRP)*<sup>[35,52–56]</sup> and the *nitroxide mediated radical polymerization (NMP)*.<sup>[57–60]</sup> These systems require adapted initiators (alkyl halides for ATRP, alkoxyamines for NMP). These initiators and the derived dormant chains reversibly produce (macro)radicals by direct activation via either a redox dissociation mechanism (ATRP, usually involving the use of a copper-based transition-metal complex catalyst) or via thermal dissociation (NMP). Both the radical concentration and the concentration of obtained living macromolecules is therefore directly determined by the concentration of the respective initiator (stoichiometric polymerization).

The most important examples for the second category—the reversible chain transfer—are the *reversible addition–fragmentation chain transfer (RAFT) polymerization*<sup>[61–64]</sup> and the *organotellurium-mediated radical polymerization (TERP)*.<sup>[65–67]</sup> These systems require the use of reversible chain-transfer agents along with the continuous production of radicals resulting from the dissociation of a classical radical initiator introduced in low concentration with respect to the control agent. Here, the chain transfer agent only determines the concentration of obtained living chains. The dormant chains are activated by an exchange mechanism with the propagating macroradicals. In the case of TERP, this exchange takes place directly; in the case of RAFT, via an addition–fragmentation step. Since the latter occupies a central role in this work, it is presented in more detail in a separate section.

**RAFT polymerization** The reversible addition–fragmentation chain transfer (RAFT) process was first presented in the year 1998 by the Australian *Commonwealth Scientific and Industrial Research Organisation (CSIRO)*.<sup>[68–70]</sup> The contemporaneously presented *Macromolecular Design via the Interchange of Xanthates*





**Scheme 1.2:** Elementary reactions in a RAFT polymerization. Z denotes the stabilizing group, R the re-initiating group, I an initiator fragment, M a monomer molecule, and P a polymer chain.

(MADIX)<sup>[71,72]</sup> polymerisation proceeds with the same reaction mechanism, but refers exclusively to xanthates (xanthic acid esters, see Figure 1.1b) as mediating agents.

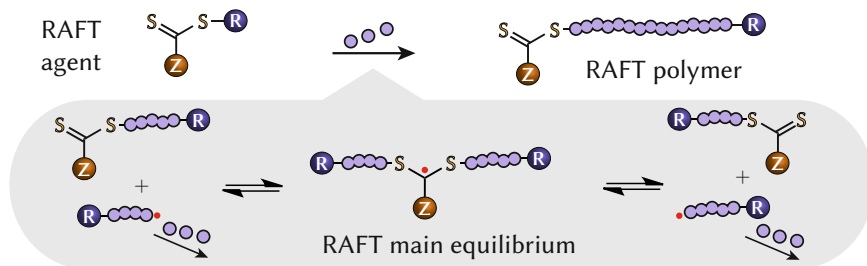
RAFT polymerization is arguably the most versatile RDRP technique: It can be performed in almost all solvents, including aqueous solutions<sup>[73,74]</sup> and supercritical fluids,<sup>[75]</sup> over a wide temperature<sup>[76,77]</sup> and pressure<sup>[78]</sup> range. The high tolerance towards functional groups<sup>[79,80]</sup> enables all common monomers which are amenable to radical polymerization (see Section 1.2.1.1) to be used for RAFT polymerizations as well,<sup>[81–83]</sup> allowing for the synthesis of a wide variety of polymeric structures with defined molar-mass distributions (see Section 1.2.1.2).<sup>[22,84–87]</sup>

As control agents<sup>[88]</sup> in RAFT polymerizations, usually compounds of the group of *dithioesters*,<sup>[89,90]</sup> including xanthates, trithiocarbonates, and dithiocarbamate compounds,<sup>[91,92]</sup> are employed. The generic chemical structure is shown in Figure 1.1a. In this figure, Z denotes the *stabilizing group*, and R the *re-initiating group*. The active group between Z- and R- group in a RAFT agent is often termed the *RAFT group*. All other components in a RAFT polymerization are identical to a conventional radical polymerization system (see Section 1.2.1.1).

In Scheme 1.2, all elementary reaction steps of the generally accepted mechanism of RAFT polymerization are presented.<sup>[93]</sup> As in the case of conventional radical polymerization, the polymerization is started by the addition of a radical to a monomer molecule (initiation). The radicals are shown here as derived from a thermal initiator, but also other initiation methods are possible.<sup>[94,95]</sup> The growing polymer chains quickly add to the reactive carbon–sulfur double bond of the RAFT agent and a tertiary radical intermediate is formed (*pre-equilibrium*). The stability of this intermediate radical is affected by the Z-group. Strongly stabilizing Z-groups promote the formation of the tertiary radical and hence increase the reactivity of the carbon–sulfur double bond.<sup>[96]</sup> This stabilization, however, must not be too strong, since the formed radical must be able to easily decompose in the next step. A typical stabilizing Z-group which is suitable for the controlled polymerization of many different monomer types is the phenyl group.<sup>[97,98]</sup> In principle, there exist two possible decomposition pathways for the intermediate RAFT-centered radical: Either the reverse reaction of the described addition takes place, which simply regenerates the initial RAFT agent and the polymer radical, or the R-group is split off and a macromolecular RAFT agent is obtained. The R-group can then re-initiate the polymerization by addition to a monomer molecule and start another growing polymer chain, which in turn adds to a RAFT agent or a macromolecular RAFT agent. The R-group must therefore be a fast-fragmenting leaving group with respect to the polymer chain, but the formed radical must also be reactive enough to quickly re-initiate the polymerization. Therefore, both Z- and R-groups must be rationally chosen in a RAFT agent to enable the polymerization of a given monomer.<sup>[99]</sup> The phase of the polymerization in which a rapid exchange of growing polymer chains and those bound to a macromolecular RAFT agent takes place is called *main equilibrium*. This exchange reaction leads to all polymer chains having approximately the same probability to grow. The result is a narrow molar-mass distribution.

At the end of the polymerization, a large majority of macromolecular chains possess the RAFT (and Z-) group at one end and the R-group at the other end.<sup>[100,101]</sup> The overarching consequence is that in a RAFT polymerization, the polymer is evenly inserted into all RAFT agents between their RAFT and R-groups. This net reaction is illustrated in Scheme 1.3 along with the underlying control mechanism in the main equilibrium. The produced macro-RAFT agents can be employed in a second radical polymerization to produce block copolymers.<sup>[102–106]</sup>

Assuming that all RAFT-agent molecules take part in the reaction and neglecting the radical chains carrying fragments of the radical initiator,<sup>[107,108]</sup> the theoretical



**Scheme 1.3:** Net reaction of a RAFT polymerization: the polymer chain is inserted between the RAFT group and the re-initiating group. Control over this reaction is provided by the RAFT main equilibrium. Z denotes the stabilizing group, R the re-initiating group. See Scheme 1.2 for the detailed elementary reactions.

number-weighted mean of the molar masses  $\overline{M}_{n,theo}$  of polymers from a RAFT polymerization can be predicted for any monomer conversion  $X_M$  via the equation:

$$\overline{M}_{n,theo} = \frac{c_M \times M_M \times X_M}{c_{RAFT}} + M_{RAFT}. \quad (1.1)$$

Here,  $c_M$  and  $c_{RAFT}$  are the concentrations of the monomer and the RAFT agent,  $M_M$  and  $M_{RAFT}$  are the respective molar masses. For polymerizations in bulk, the product of the monomer's concentration and molar mass approximately coincides with its density  $\delta_M$ :

$$c_M \times M_M \approx \delta_M. \quad (1.2)$$

Insertion of (1.2) into (1.1) gives:

$$\overline{M}_{n,theo} \approx \frac{\delta_M \times X_M}{c_{RAFT}} + M_{RAFT}. \quad (1.3)$$

**The trithiocarbonate group** Trithiocarbonates (Figure 1.1c) are among the most commonly used RAFT agents. They are relatively easy to synthesize and very versatile—they control polymerizations with a variety of monomers.<sup>[61,109]</sup> Trithiocarbonates are unique RAFT agents in the sense that they are inherently bifunctional, so that a polymer chain can be inserted on both sides of the functional group when it is connected to two good leaving groups, and the trithiocarbonate group will be found in the middle of the formed polymer chains.<sup>[110]</sup> Triblock copolymers can thus be prepared in just two polymerization steps.<sup>[111,112]</sup>

Organic trithiocarbonates are typically synthesized by reaction of thiols with carbon disulfide in alkaline medium.<sup>[113–116]</sup> An alternative method is the reaction of trithiocarbonate anions with alkyl halogenides<sup>[117–120]</sup> or alkyl tosylates<sup>[121]</sup> in the presence of bases,<sup>[122,123]</sup> phase-transfer catalysts,<sup>[124,125]</sup> or elevated temperatures.<sup>[126]</sup> The trithiocarbonate anion for these reactions, which follow the mechanism of a nucleophilic substitution, can be prepared *in situ* by treatment of carbon disulfide with bases.<sup>[127]</sup> In this work, most of the used RAFT agents are of trithiocarbonate type.

### 1.2.1.2 Molar-mass distributions

The degrees of polymerization (and therefore also the molar masses) in polymer materials are not identical for all macromolecules, but distributed over a certain range. In order to describe this distribution of chain lengths, usually a *distribution function*<sup>\*</sup> is given, by which the relative frequency of respective molecules can be calculated for all chain lengths in the material. Because the molar mass can only assume certain values, all these functions are discreet.

It is advisable to give any distribution function in normalized form, in order to render it independent of the number of macromolecules, which means that the sum over all function values  $\underline{M}_i$  must be equal to 1:

$$\sum_{i=1}^{\infty} \underline{M}_i = 1. \quad (1.4)$$

To transform any distribution function  $x(M)$  into the normalized form  $\underline{x(M)}$ , it has to be divided by the sum of all possible function values, the normalization factor  $N$ :

$$\underline{x(M)} = \frac{x(M)}{N}, \quad (1.5)$$

$$N = \sum_{i=1}^{\infty} M_i. \quad (1.6)$$

Distribution functions are often stated in terms of the degree of polymerization  $p$ , rather than the molar mass  $M$ . The degree of polymerization is the proportionality factor between the molar mass  $M$  of the complete polymer chain and the molar

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<sup>\*</sup>This should not be confused with the *cumulative distribution function* in statistics which describes the probability that a random variable will be found at a value less than or equal to the corresponding function variable. The term “distribution function” is strictly used in the sense of a *probability mass function* in this work.

mass of the monomeric unit  $M_M$ , so that a given distribution function can be easily converted into a *chain-length distribution function* using the following equation:

$$M = p \times M_M. \quad (1.7)$$

For a chain-growth polymerization, for which the assumptions can be made that the number of growing chains remains constant, the addition of monomer molecules does not depend on the chain length, and that the growth of all chains is stated at the same time—this holds true for reversible-deactivated radical polymerizations—the molar mass distribution of the produced macromolecules can be expressed by a *Poisson distribution*.<sup>[128]</sup> The (normalized) Poisson distribution  $N_p^P$  as a function of the degree of polymerization  $p$  with an expectation value of  $v_p$  is

$$N_p^P = \frac{v_p^p \times e^{-v_p}}{p!}, \quad p = 1, 2, 3, \dots \quad (1.8)$$

**Characterization of molar mass distributions** Statistical quantitative key measures of distribution functions are generally expressed as the *moments* of these distributions. The  $v^{\text{th}}$  *moment about the mean*  ${}^n\mu_v$  (or  $v^{\text{th}}$  *central moment*) of an integer-valued random variable  $i$  with the distribution function  $N_i$  is defined as

$${}^n\mu_v \equiv \sum_{i=1}^k N_i \times M_i^v, \quad v \in \mathbb{Z}, \quad (1.9)$$

$k$  being the highest occurring value. The zeroth central moment  ${}^n\mu_0$  of a normalized distribution function is 1, otherwise it coincides with the normalization factor  $N$  (see Equation (1.6)).

The quotient of the first and the zeroth moment of a molar mass distribution equals the arithmetic mean of all molar masses  $M_i$ , which are weighted by their absolute frequencies  $n_i$ . This mean value is called *number average*  $\overline{M}_n$  of the molar mass,

$$\overline{M}_n \equiv \frac{{}^n\mu_1}{{}^n\mu_0} \stackrel{(1.9)}{=} \frac{\sum_{i=1}^k N_i M_i}{\sum_{i=1}^k N_i}. \quad (1.10)$$

It is accessible experimentally, for example, by osmometry.

The mean value of all molar masses of a sample, which are weighted by the corresponding mass  $m_i$ , is the so-called *mass average*  $\overline{M}_w$  of the molar mass,

$$\overline{M}_w \equiv \frac{\sum_{i=1}^k m_i M_i}{\sum_{i=1}^k m_i}. \quad (1.11)$$

The absolute mass  $m_i$  corresponds to the product of the number  $n_i$  of macromolecules and their molar mass  $M_i$ :

$$m_i = n_i M_i. \quad (1.12)$$

Insertion of (1.12) in (1.11) shows that the mass average  $\overline{M}_w$  is the quotient of the second and the first moment of the number-weighted molar mass distribution:

$$\overline{M}_w = \frac{\sum_{i=1}^k n_i M_i^2}{\sum_{i=1}^k n_i M_i} = \frac{\sum_{i=1}^k N_i M_i^2}{\sum_{i=1}^k N_i M_i} \stackrel{(1.9)}{=} \frac{{}^n\mu_2}{{}^n\mu_1}. \quad (1.13)$$

In the case where all macromolecules possess the same mass, the number average and the mass average of the molar mass distribution are identical. Otherwise, the mass average is always higher:

$$\overline{M}_w \geq \overline{M}_n. \quad (1.14)$$

A method which gives access to the mass average is static light scattering.

An important indicator for the characterization of the width of molar mass distributions is the *dispersity*  $\mathcal{D}$  (formerly called *polydispersity index*, *PDI*). It is defined as the quotient of mass average and number average of the molar mass distribution:\*

$$\mathcal{D} \equiv \frac{\overline{M}_w}{\overline{M}_n} \stackrel{(1.10)}{=} \frac{{}^n\mu_2}{{}^n\mu_1} \stackrel{(1.13)}{=} \frac{{}^n\mu_2}{{}^n\mu_1^2}, \quad \mathcal{D} \geq 1. \quad (1.15)$$

A narrow molar mass distribution possesses a low  $\mathcal{D}$ , which is desirable for most purposes.

For the Poisson distribution, the mean value of the number distribution  $\overline{M}_n^p$  coincides with its expectation value  $\nu_p$ :

$$\overline{M}_n^p = \nu_p. \quad (1.16)$$

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\* Due to the proportionality of molar mass and degree of polymerization, the dispersity  $\mathcal{D}$  can as well be calculated by inserting distribution functions of the degree of polymerization here.

The mass average  $M_w^P$  of the Poisson distribution is

$$\overline{M}_n^P = \nu_p + 1. \quad (1.17)$$

The dispersity  $\mathcal{D}^P$  of the Poisson distribution is therefore

$$\mathcal{D}^P \stackrel{(1.15)}{=} \frac{\overline{M}_w^P}{\overline{M}_n^P} \stackrel{(1.16)}{\stackrel{(1.17)}}{=} \frac{\nu_p + 1}{\nu_p} = 1 + \frac{1}{\nu_p}. \quad (1.18)$$

With growing expectation value, the dispersity of the Poisson distribution decreases and converges to the value of  $\mathcal{D} = 1$ .

**Size-exclusion chromatography** The most important method for the determination of molar mass distributions of polymers is *size-exclusion chromatography*<sup>[129,130]</sup> (SEC), also termed *gel-permeation chromatography*<sup>[131,132]</sup> (GPC) when organic solvents are used. It is a form of liquid chromatography, performed as column chromatography.

The stationary phase consists in a porous, swollen polymer network with a broad distribution of pore sizes. The fractionation is based on the different hydrodynamic volume  $V_h$  of the analytes, which can be calculated from the intrinsic viscosity  $[\eta]$  and the molar mass  $M$  by

$$V_h = [\eta] \times M. \quad (1.19)$$

Polymers dissolved in a solvent increase its viscosity. The reduced viscosity  $\eta_{\text{red}}$  expresses the contribution of the polymer to the total viscosity:

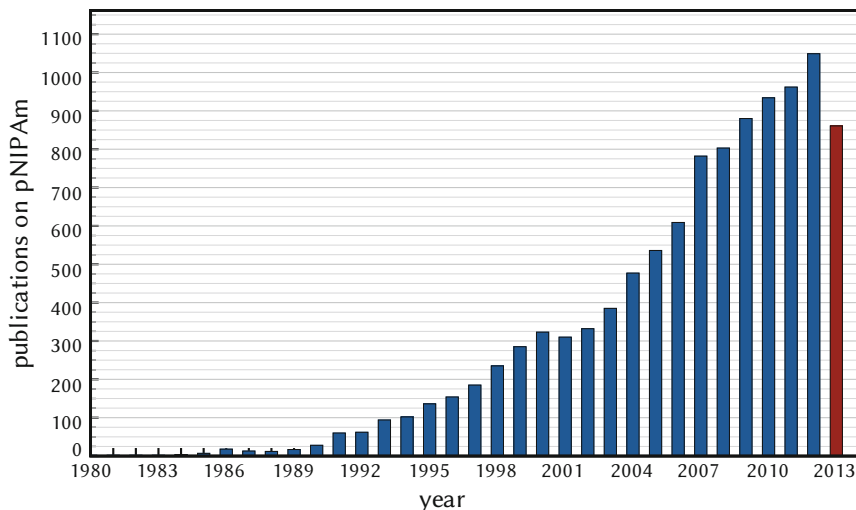
$$\eta_{\text{red}} = \frac{\eta_c - \eta_s}{\eta_s}. \quad (1.20)$$

Here,  $c$  is the polymer's concentration,  $\eta_c$  the viscosity of a polymer solution with the concentration  $c$ , and  $\eta_s$  the viscosity of the pure solvent. Extrapolation to very low concentrations yields the intrinsic viscosity  $[\eta]$ , which is also called *Staudinger index*:

$$\lim_{c \rightarrow 0} \eta_{\text{red}} = [\eta]. \quad (1.21)$$

The higher the hydrodynamic volume of the analyte particle, the lower is its retention time in the column.

SEC is a relative method and any instrument has therefore to be calibrated with calibration samples having very narrow and known molar mass distributions.<sup>[133]</sup> When no calibration data are available for a given substance, it is possible to use



**Fig. 1.2:** Temporal development of the number of new publications on pNIPAm per year. The data were obtained from WEB OF KNOWLEDGE running a search for the name of the polymer and all common acronyms in the title or the keywords. The search was performed in November 2013.

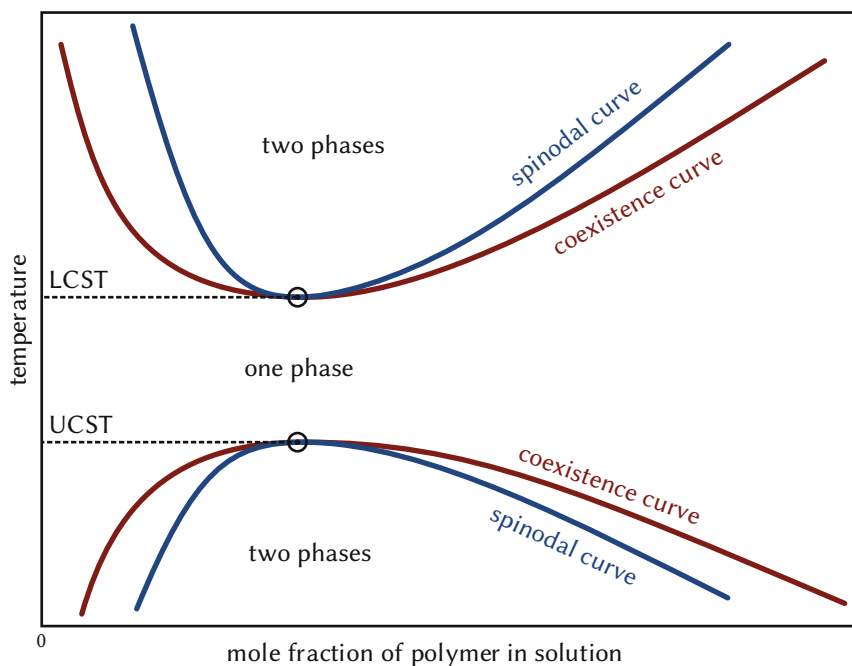
a universal calibration, when the *Mark-Houwink parameters* are known.<sup>[134]</sup> The results of SEC measurements are typically either given as mass-weighted molar-mass distributions in logarithmic form  $W(\log M)$ , when a calibration could be applied,<sup>[135]</sup> or as the directly obtained chromatograms as a function of the retention time.

### 1.2.2 Poly(*N*-isopropylacrylamide) (pNIPAm)

The central role for the presented work of *poly(N-isopropylacrylamide)* (pNIPAm) and its special characteristic features in aqueous solution, namely thermoresponsive properties (Section 1.2.2.1) and cononsolvency (Section 1.2.2.2), justify dedicating a stand-alone theoretical section to this polymer.

PNIPAm is typically prepared from the respective monomer (see Figure 5.11) by radical polymerization.<sup>[136]</sup> The polymer is the topic of over 10 000 publications, mostly from polymer and materials science and chemistry, but also in great part from other fields like physics, biology, medicine and pharmacology. The number of publications per year is thereby steadily increasing. It already exceeded 1000 in 2012 and the increase does not seem to have peaked yet, as it can be seen in the





**Fig. 1.3:** Exemplified schematic phase plot of a typical polymer binary solution phase behavior featuring both a lower critical solution temperature (LCST) and an upper critical solution temperature (UCST). The coexistence curve is also termed “binodal curve”.

plot in Figure 1.2. In some of these studies, pNIPAm was just used because of its solubility in water and almost all polar organic solvents. Other studies cover practical applications of pNIPAm, such as tissue engineering,<sup>[137]</sup> electrophoresis,<sup>[138]</sup> or chromatography.<sup>[139]</sup> The majority of studies, however, deal with the very special behavior of the polymer in aqueous solutions, which is contrary to most other polymers and described in the following.

### 1.2.2.1 PNIPAm as a smart polymer

**Solubility of polymers in general** First of all, the effect of the temperature on the solubility of polymers shall be discussed in general. Figure 1.3 shows a schematic temperature-dependent phase diagram of a polymer binary solution exhibiting two characteristic features: The system is miscible at all compositions

at medium temperatures, but the polymer precipitates when the temperature is raised or decreased. Two special points are marked in this diagram: The lowest temperature at which the system is miscible for all possible compositions is called *upper critical solution temperature (UCST)* and the highest temperature at which the system is miscible independent of the composition is called *lower critical solution temperature (LCST)*.<sup>[140]</sup> Describing these phenomena in thermodynamic terms, it can be stated that for the components of a system to be miscible, the increment of the free enthalpy (Gibbs energy) of mixing  $\Delta G_{\text{mix}}$  has to be negative:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0. \quad (1.22)$$

$\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  are the increments of the enthalpy and entropy of mixing,  $T$  is the absolute temperature.

In the case of a UCST, this expression becomes negative with increasing temperature. That means that both the increments of the enthalpy and the entropy of mixing necessarily have to be positive:

$$\text{UCST:} \quad \Delta H_{\text{mix}} > 0, \Delta S_{\text{mix}} > 0. \quad (1.23)$$

In the case of an LCST, the increments of the enthalpy and the entropy of mixing both have to be negative:

$$\text{LCST:} \quad \Delta H_{\text{mix}} < 0, \Delta S_{\text{mix}} < 0. \quad (1.24)$$

For completeness, also the two remaining possibilities shall be considered. If

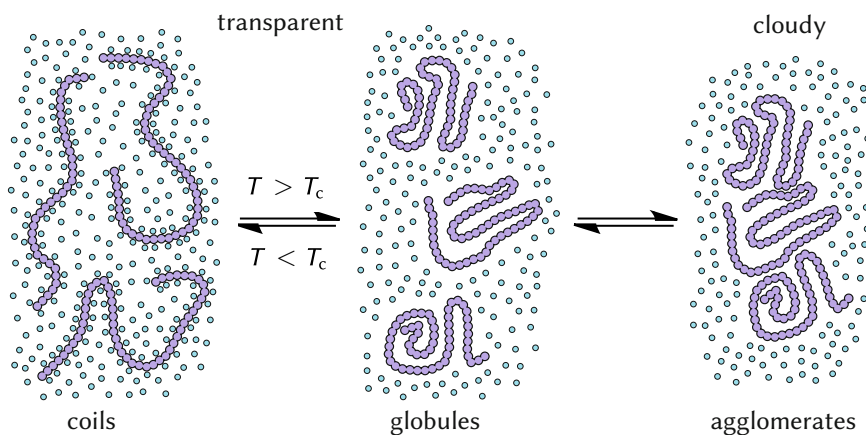
$$\Delta H_{\text{mix}} < 0, \text{ and } \Delta S_{\text{mix}} > 0, \quad (1.25)$$

the polymer is soluble at all temperatures, and if

$$\Delta H_{\text{mix}} > 0, \text{ and } \Delta S_{\text{mix}} < 0, \quad (1.26)$$

the polymer is insoluble at all temperatures, obviously given that  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  are themselves temperature-independent.

A UCST behavior is the standard behavior in organic solvents with undirected intermolecular forces and clearly more common for polymer solutions than an LCST behavior. In fact, the existence of an LCST is counterintuitive since it requires a negative entropy of mixing, that is, the system becoming more “ordered” upon mixing. The key of understanding here is the low *orientation entropy*<sup>[141]</sup> in the solution. Highly ordered structures are formed by the solvent molecules around the polymer chains, driven by their enthalpy of formation. When the polymer



**Scheme 1.4:** Schematic illustration of the clouding of a polymer solution by the coil-to-globule transition. The aggregation of the globules causes the solution to appear opaque.

precipitates endothermically, these aggregates collapse, accompanied by an increase of the total entropy.<sup>[142]</sup> It goes without saying that this behavior is almost exclusively observed for solutions with very polar solvents (usually water) which are able to have specific (directed) interactions with the polymer, namely oriented hydrogen bonds.

Of course, in principle most systems would show mixing and demixing at some point, but in practice, with many systems one does not observe phase separation upon cooling, because the solvent solidifies before it becomes sufficiently poor to induce demixing. Analogously, the solvent often boils at atmospheric pressure before the two-phase state is reached.

**Coil-to-globule transition of pNIPAm** It has been known since 1968<sup>[143]</sup> that aqueous solutions of pNIPAm exhibit an LCST at around 32 °C (atactic polymer with  $\bar{M}_n > 10^4 \text{ g mol}^{-1}$ <sup>[144]</sup> at atmospheric pressure).<sup>[145,146]</sup> Below that temperature, the polymer chains are in the hydrated state. Water molecules are associated with the amide groups by hydrogen-bonding,<sup>[147]</sup> and additionally form cage-like structures<sup>[148]</sup> around the hydrophobic isopropyl groups along the polymer chain.<sup>[149]</sup> Because the polymer cannot form hydrogen bonds with itself, the dissolution is energetically favored. The solution appears completely transparent.

When the cloud temperature\*  $T_c$  is exceeded, the expanded polymer coils collapse to shrunken globules in an endothermic coil-to-globule transition.<sup>[151,152]</sup> The segregated polymer globules subsequently aggregate. This in turn renders the solution turbid, due to the different refractive indices of the components, or potentially even visible flocks and a two-phase system are formed. (The coil-to-globule transition itself does not change the visual appearance of the solution.) The clouding of a pNIPAm solution above the cloud temperature is illustrated schematically in Figure 1.4. The major driving force for the coil-to-globule transition is the dehydration of the hydrophobic moieties.<sup>[153]</sup> In solution, there are around 8–15 water molecules per monomer unit associated with the polymer chain.<sup>[154–156]</sup> Above the cloud temperature, this number drastically drops to almost zero—the polymer becomes hydrophobic.

Strictly speaking, the LCST is only the *critical* temperature at the minimum of the two-phase region for a certain polymer concentration, the temperature below which the components of a mixture are miscible for all compositions. But in the case of pNIPAm in water, the spinodal curve (see Figure 1.3) is very flat and increases only a few degrees, when going from the minimum concentration at which the turbidity is still observable up to very high concentrations.<sup>[157]</sup> (So flat, it is very hard to give an exact composition corresponding to the LCST. It is around 5–10 % by weight.)<sup>[147]</sup> Consequently, people often refer to the transition temperature at any composition as the LCST. This is nevertheless a bad habit and should be avoided.

Due to the abruptness and reversibility of the thermoresponsive transition, pNIPAm is counted among the group of *smart polymers*,<sup>[158,159]</sup> also termed *stimuli-responsive*,<sup>[160,161]</sup> *intelligent*,<sup>[139]</sup> or *environmentally sensitive*.<sup>[162]</sup> These polymers react to one or more external physical (temperature, pressure, radiation), chemical (pH value, signaling molecules) or biological (enzymes) stimuli with drastic changes in their chemical and physical properties. Important features are that these changes are drastic, discontinuous, and reversible. That means that the changes occur abruptly at a certain point, but the material returns to its initial state upon application of a counter-trigger. Aqueous pNIPAm solutions are arguably the most prominent representative of the class of smart polymers and have been established as the standard model system to study the coil-to-globule transition,<sup>[163,164]</sup> which is of great importance for biology because of the presence of coil-globule transitions of proteins, nucleic acids and other biopolymers.<sup>[165]</sup> These natural macromolecules are stable in solution over a wide range of stimuli, but react at a certain point with drastic conformational alteration and concomitant changes of their properties.<sup>[166]</sup> Another

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\*This term is preferred over “transition temperature” because it refers to the observable phenomenon of the clouding of the solution, which is generally taken as optical indicator for the determination of this temperature.<sup>[150]</sup>

thermoresponsive polymer is for instance poly(*N*-vinylcaprolactam).<sup>[167]</sup> Examples of pH-responsive polymers are poly(2-(diethylamino)ethyl methacrylate)<sup>[168]</sup> and poly(2-(dimethylamino)ethyl acrylate) (pDMAEA).<sup>[169]</sup> The reactions of smart polymers to their external stimuli can be fine-tuned by factors such as the concentration, the chain-length distribution, the topology, or additives. For pNIPAM, most additives to the aqueous solution lower the cloud temperature.<sup>[170–173]</sup> For inorganic salts, the lowering effect can be correlated with the Hofmeister series,<sup>[174]</sup> in which the ions were originally sorted according to their strength in precipitating (“salting out”) proteins from aqueous solutions.<sup>[175,176]</sup> By the synthesis of block copolymers, the desirable properties of two different types of polymers can often be combined.<sup>[177]</sup>

PNIPAm can be crosslinked to form a hydrogel. Typical crosslinkers are *N,N'*-methylene-*bis*-acrylamide and *N,N'*-cystamine-*bis*-acrylamide.<sup>[178,179]</sup> Here, heating and cooling lead to the reversible collapsing or swelling of the hydrogels.<sup>[179]</sup> The transition still occurs at a temperature approximately identical to the cloud temperature of isolated chains—coined the “volume phase transition temperature” for hydrogels. That means that most results obtained for isolated chains can be applied correspondingly to crosslinked pNIPAm.<sup>[180]</sup> These hydrogels show great potential for applications in medicine,<sup>[158]</sup> in particular for drug delivery<sup>[181–183]</sup> in biomedical engineering because the transition occurs just below the human body temperature and accompanied by an expulsion of any absorbed therapeutics.<sup>[160,161]</sup>

### 1.2.2.2 Cononsolvency

The second very particular feature of aqueous pNIPAm solutions is the very rare phenomenon of *cononsolvency*, which shall be explained in the following. The term derives from the clearly more common phenomenon of *cosolvency*<sup>[184,185]</sup> (also called *mixed* or *true* cosolvency) which was found and coined independently by Wolf and Molinari<sup>[186]</sup> (1973) and Cowie and McEwen<sup>[187]</sup> (1974) for the ternary system polystyrene in acetone and diethyl ether. Another example is the system of poly(methyl methacrylate) (pMMA) in water and methanol. The IUPAC gives the following definition for cosolvency of polymers\* in the “IUPAC Gold Book”:<sup>[188]</sup>

*Co-solvency (in polymers):*

The dissolution of a polymer in a solvent comprising more than one

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\*It should be noted that the definition is different in pharmaceuticals, where the word cosolvent is used for a solvent which also dissolves the drug in pure form. Also, cosolvency is just the special case for mixtures of one solid and two liquid substances. A more general term would be co-miscibility, although that term is very uncommon.

component, each component of which by itself is a non-solvent for the polymer.\*

Cononsolvency is simply the contrary phenomenon—the formation of a nonsolvent for a polymer by mixing two solvents.<sup>[189]</sup>

For pNIPAm, it was first reported for by Winnik, Ringsdorf, and Venzmer<sup>[190]</sup> in a communication in 1990 (although the equivalent effect for pNIPAm hydrogels was already known by then).<sup>[180,191,192]</sup> In reading an article by Schild and Tirell<sup>[193]</sup> on the measurement of the cloud temperature of pNIPAm with calorimetry and they stumbled over a sentence in the experimental section where the precipitation of the polymer from the aqueous polymerization solution was mentioned:

Precipitation was carried out by dropwise addition of the polymerization mixture to 800 mL of methanol.

It surprised them that the precipitation of pNIPAm was performed by its addition to the even better solvent methanol, which probably goes against the natural intuition of any synthetic chemist. (In terms of solubility in mixtures of water and methanol, pNIPAm is just the opposite to the above-mentioned pMMA.) After reproduction of the experiment with different mole fractions of methanol, they published the aforementioned communication and were thus even faster with their publication than the authors of the paper they had originally read, who published the same results, albeit with more detailed experiments, shortly after.<sup>[194]</sup>

In the following years, this anomaly was analyzed in further detail by different scientists in over 100 publications, varying lots of different factors.<sup>[195,196]</sup> It was found for example that, unlike for the cloud temperature of pure aqueous pNIPAm solutions, the cononsolvency area does depend very strongly on the polymer's molar masses.<sup>[197]</sup> This is important to note since before the advent of RDRP (see Section 1.2.1.1), only samples with very ill-defined molar masses from conventional radical polymerization were accessible for research, so that only quite inaccurate results were achievable which could not be easily aligned with theoretical expectations.

The miscibility gap in the system with methanol as cononsolvent is treated in the majority of studies,<sup>[198–200]</sup> but also several other common organic solvents act as cononsolvents for aqueous solutions of pNIPAm, including other alcohols,<sup>[191,201]</sup> dimethyl sulfoxide (DMSO),<sup>[202]</sup> *N,N*-dimethylformamide (DMF),<sup>[203]</sup> dioxane<sup>[204]</sup> tetrahydrofuran (THF),<sup>[205]</sup> acetone, and others.<sup>[201]</sup> In some of these cases, the LCST behavior can be retained over the whole composition range, as for methanol or

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\*The spelling is retained in the quote, although it differs from the (more commonly used) spelling in this work.

acetone as cononsolvents. In contrast, the phase-separation curve in a temperature-mole fraction phase diagram can also be flipped for higher mole fractions of the organic cononsolvent, such that heating of the mixture leads to the solution clearing up (UCST behavior). Examples for this behavior are DMSO or ethanol as cononsolvents.<sup>[206]</sup> As for the temperature-induced clouding described above, the results regarding cononsolvency of linear pNIPAm chains directly apply to the crosslinked polymer as well.<sup>[207]</sup> The hydrogels shrink upon addition of a cononsolvent and expel the absorbed molecules.

Possible explanations for the cononsolvency of these systems are still vigorously discussed in the scientific community. In essence, it is categorically disputed whether this intriguing anomaly can be mainly traced to polymer-solvent or to solvent-solvent interactions. Both models, which are mutually incompatible, have strengths and weaknesses in explaining and predicting the behavior:

**Polymer-solvent interactions:** According to this first theory, the cononsolvent competes with the water for the hydrogen-bond positions,<sup>[208]</sup> preferentially binds to the polymer,<sup>[195,209,210]</sup> and replaces the associated water molecules. In these aggregates, the hydrophobic part of the cononsolvents points towards the solution, making the polymer hydrophobic overall and therefore insoluble until the solvent mixture becomes hydrophobic enough to enable solvency by nonspecific interactions after further addition of the cononsolvent.<sup>[211]</sup> This explanation seems most reasonable for cononsolvents like alcohols, which are able to actively form hydrogen-bonds and possess a hydrophobic tail. In fact, this model of competitive hydrogen bonding refers in most cases to the system pNIPAm/water/methanol.<sup>[195]</sup> Here, it is supported by several theoretical calculations.<sup>[197,212,213]</sup>

**Solvent-solvent interactions:** According to the second model of solvent-solvent interactions, energetically favorable complexation forms network or cluster structures<sup>[214,215]</sup> in the liquid mixture.<sup>[151]</sup> For the system pNIPAm/water/methanol, it is for example speculated that water pentamers are formed with methanol by hydrogen bonding,<sup>[216]</sup> but most of the formed structures have only been predicted theoretically, since they are very hard to detect experimentally with currently used methods.<sup>[214,217]</sup> These structures are then assumed to be poorer solvents for the polymer than the two pure solvents.<sup>[216,218-220]</sup> Put simply, there are just less water molecules available to hydrate the polymer.<sup>[206]</sup> This model is very well compatible with the finding that the solvency increases again when ions are added which are known to destroy the postulated solvent-solvent complexes.<sup>[196]</sup> On the other hand, it also displays some shortcomings, as it fails for example to explain findings

like the high influence of the polymer's molecular weight on the expansion of the miscibility gap found for methanol as cononsolvent.<sup>[197]</sup> According to this model, the solubility of polymer chains should be rather independent of their lengths.

Models involving ternary complexation interactions with structures formed by both solvents and the polymer<sup>[180,191,192]</sup> can be excluded since the transition also occurs in extremely diluted polymer solutions at the same mole fraction of cononsolvent.<sup>[149,151]</sup> Also, concentration fluctuations can be neglected as reason for cononsolvency, since, as a good approximation, most solvent mixtures can be considered as homogeneous. They can only play a major role for solvent pairs with bad miscibility.<sup>[221]</sup> It is, of course, possible that different mechanisms or combined mechanisms are responsible for the cononsolvency of different systems.

Aqueous solutions of pNIPAm are by far the best known and most studied system regarding cononsolvency. Together with the coil-to-globule transition, this makes them the number one model system for two different phenomena and underlines again the great importance of this polymer in modern research.<sup>[196]</sup>

Only very few other systems that exhibit cononsolvency behavior are known. Most of the examined systems comprise copolymers of NIPAm and other monomers with a very high content of pNIPAm,<sup>[222]</sup> but there are also a few other examples:

- poly(*N*-isopropylmethacrylamide) in water and ethanol,<sup>[223]</sup>
- poly(2-methacryloxyethyl phosphorylcholine) in water and ethanol<sup>[224]</sup> or 2-propanol,<sup>[225]</sup>
- poly(vinyl alcohol)<sup>[226,227]</sup> and poly(*N,N*-diethylacrylamide) in water and DMSO<sup>[192]</sup> or methanol,<sup>[228]</sup>
- poly(*N,N*-dimethylacrylamide) in water and organic solvents,<sup>[229]</sup>
- poly(vinyl methyl ether) in water and alcohols<sup>[230]</sup> or THF,<sup>[231]</sup>
- poly(vinylpyrrolidone) in water and methanol,<sup>[232]</sup>
- poly(oligo(ethylene glycol)-phenyl ether acrylate) in water and ethanol,<sup>[233]</sup>
- cellulose acetate in acetic acid and aniline,<sup>[190]</sup>
- polystyrene in DMF and cyclohexane,<sup>[189]</sup>
- poly(ether imide) in *N*-methyl-2-pyrrolidinone and methylene chloride<sup>[234]</sup>



- poly(methyl methacrylate) in chlorobutane<sup>[235]</sup> and amyl acetate and in pyridine and formic acid,<sup>[236]</sup>
- poly( $\eta$ -caprolactone) in pyridine and formic acid.<sup>[236]</sup>

Many of these systems, especially the latter non water-soluble polymers, exhibit only a UCST-style cononsolvency behavior that is totally different from the LCST-cononsolvency behavior of pNIPAm.<sup>[204,229]</sup> Often, the type of behavior is not even discussed or examined. Moreover, the solution does not necessarily become turbid at the structural transition of the polymer.<sup>[232]</sup> Again, this highlights the particularity of pNIPAm in polymer science.

### 1.2.3 Nanosciences

Nanosciences is the generic term for any aspect of science in which objects with features on the multi-nanometer length scale are synthesized or studied. When speaking about the macroscopic properties of such substances, people often refer to them as *nanomaterials*. A more functionality-based definition of nanomaterials, which is dependent on the type of the respective substance, is that their properties scale with the size of their components. Nanoparticles, the fragments of nanomaterials, are tiny in comparison to our macroscopic world, but gigantic with respect to the atoms and molecules which are at the center of traditional chemistry. Consequently, in their properties, they are fundamentally distinct and unique, giving rise to a wide range of potential applications (also see the Introduction, Section 1.1).

It should also be mentioned at this point that, as is arguably the case for any emerging technology, nanosciences raise many concerns in parts of our society, ranging from worries about the environmental impact and the toxicity of nanomaterials<sup>[237–241]</sup> through to apocalyptic doomsday scenarios, such as the fear of an earth-consuming “gray goo”, composed of self-replicating nanorobots gone out of control.<sup>[1]</sup> On the other hand, people have in principle been unknowingly using nanotechnology since ancient times. A good example (other than the gold-stained glass objects in Figure 1.4) was recently presented by Reibold *et al.*<sup>[242]</sup> (2006). They were able to show that the mythical quality of blades made of “Damascus steel”, produced in ancient India using high-carbon steel and first encountered by the crusaders when fighting against Muslims, can—at least in part—be traced to incorporated carbon nanotubes and cementite nanowires, which had formed within the historical, but today no longer replicable, production process.

### 1.2.3.1 General strategies for the synthesis of nanomaterials

Very broadly, there are two general approaches to reach the nanoscale: the *bottom-up* and the *top-down* approach.<sup>[243]</sup> The terms *synthesizing-up* and *engineering-down* are also in use within this context. Not only are the latter terms more figurative, they are also more specific because they exclusively refer to nanosciences. Engineering down to the nanoscale involves using the same methods which an engineer or artisan performs on the macroscopic scale, but using the latest in modern specialized techniques in order to miniaturize. A typical example is the production of electronic components with ever-decreasing sizes by lithographic etching of silicon semiconductors. Modern microchips can be made so compact that several billion transistors fit on an area as small as  $1\text{ cm}^2$ . The width of each conducting line in these integrated circuits has already dropped below 100 nm. The fabrication of microchips has therefore reached the domain of nanotechnology by going smaller and smaller, following an engineering-down strategy. In contrast, the synthesizing-up approach is modeled on biology, where nanostructures are typically reached by self-assembly of yet smaller building units. Following this approach, these building units are generally sought to be synthesized by chemical reactions, often starting from very small molecules or even individual atoms or atomic ions. To stick with the example of modern computing, the first reports of molecular computing based on supramolecular species have already begun to appear.<sup>[244]</sup>

Applying the above definitions, all synthesis strategies of nanostructures followed in this thesis can strictly be allocated to the field of bottom-up synthesis.

### 1.2.3.2 Gold nanoparticles

*Gold nanoparticles (AuNPs)*<sup>[249–251]</sup> is the generic but vague umbrella term for a variety of nanosized gold objects with greatly differing chemical and physical properties, such as color, bonding and aggregation characteristics, electronic structure, stability, dispersability, and interactions with biological systems. Most importantly, these properties depend on their size. In this regard, AuNPs can be roughly classified into *gold nanoclusters* and *gold nanocrystals*.<sup>[252,253]</sup> The terms reflect the fact that the AuNP structure becomes crystalline when the diameter exceeds a value of approximately 2 nm. The characteristic properties of the two types of nanosized gold particles are confronted in Table 1.1. Put simply, gold nanoclusters behave more like large molecules and gold nanocrystals are more comparable to tiny gold lumps.

While Michael Faraday<sup>[254]</sup> (1857) is generally regarded as the inventor of AuNP synthesis,<sup>[255]</sup> colloidal gold has been used since ancient times as a means for staining glass (see next section). In Figure 1.4, three photographs of historical gold-stained

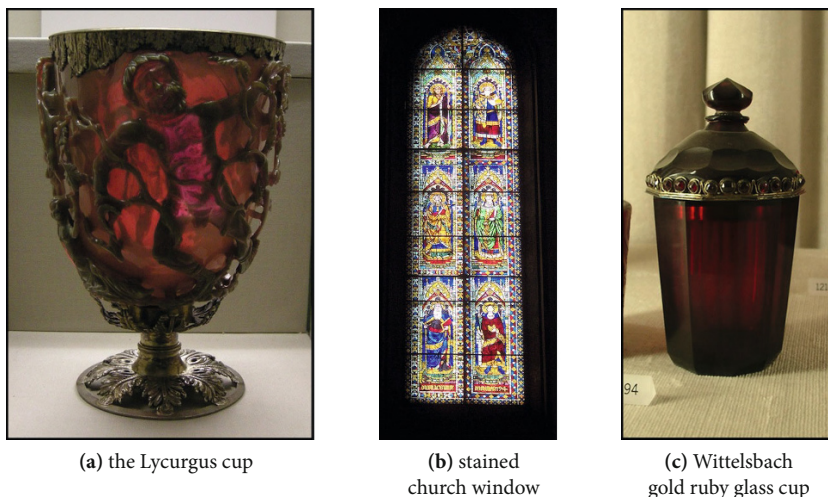
**Tab. 1.1:** Comparison of typical characteristic properties of gold nanoclusters and gold nanocrystals.

characteristic	gold nanoclusters	gold nanocrystals
diameter	< 2 nm	2.5–100 nm
number of atoms	10–100, preferentially “magic numbers”	> 200
structure	molecular-like	metallic nature (face-centered cubic)
optical spectrum	discrete electronic transitions, “fingerprint”	broad localized plasmon resonance absorption peak
resulting color	brown, yellow	red to blue (if spherical)
shapes	defined, polyhedral	many different shapes: spheres, rods, <sup>[245]</sup> cubes, <sup>[246]</sup> plates, cages, <sup>[247]</sup> rosettes, <sup>[248]</sup> ...

glass objects are shown. Photograph (a) shows the Lycurgus cup, a 4<sup>th</sup> century Roman chalice made of dichroic\* glass impregnated with gold and silver nanoparticles (approximately 70 nm),<sup>[256]</sup> today on display at the British Museum, London, UK. When the Lycurgus cup is viewed under normal lighting conditions, it appears green, but when light is shone through the glass, only the characteristic crimson color is let through. The photograph is taken in a way that both colors can be seen at the same time. Photograph (b) in Figure 1.4 shows a stained glass window from the 14<sup>th</sup> or the 15<sup>th</sup> century in the Basilica di Santa Maria del Fiore, Florence, Italy. In photograph (c), a gold ruby cup from the treasury chamber of the Wittelsbacher (Munich Residenz) can be seen. It is attributed to the German chemist and apothecary Johannes Kunckel.

On a side note, Chen *et al.*<sup>[257]</sup> (2008) have found very recently that gold-stained glass is not only pleasant to look at, but actually environmentally beneficial as well, because the enhanced magnetic field around the embedded nanoparticles' surface, which is enhanced by the irradiation with light (see next section) greatly accelerates

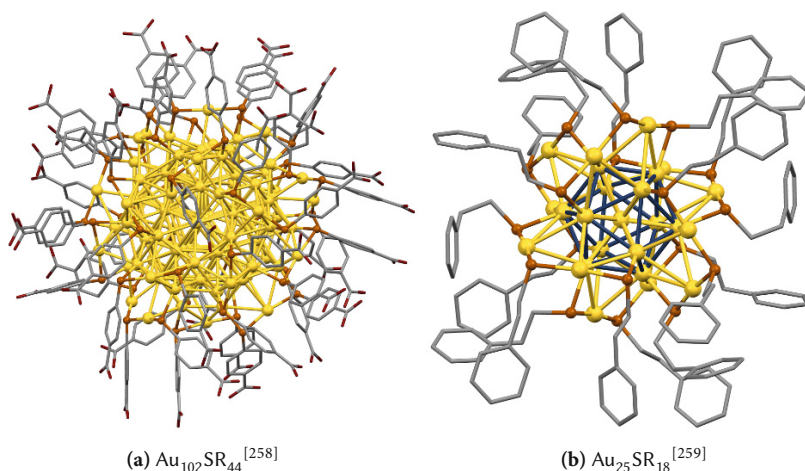
\* A *dichroic* material causes visible light to be split up into two distinct beams of different wavelengths.



**Fig. 1.4:** Photographs of historic glass objects stained with colloidal gold; photo (a) by “Sailko”, photo (b) by “JoJan”, photo (c) by “Schtone”, Wikimedia Commons under CC BY-SA 3.0.

the decomposition reaction of volatile organic pollutant compounds in the air even at ambient temperatures, therefore effectively leading to a cleansing of the air.

AuNPs are usually protected by an outer ligand layer. The typical link between the particle and the organic ligand molecules is the gold–thiolate bond.<sup>[260,261]</sup> Thanks to the higher stability of gold nanoclusters with certain “magic numbers” of gold atoms, Jadzinsky *et al.*<sup>[258]</sup> (2007) and Zhu *et al.*<sup>[259]</sup> (2008) managed to obtain gold nanoclusters in pure form, crystallize them, and determine the crystal structures by X-ray diffraction. These two structures are depicted in Figure 1.5, because they give a clear image of the type of the bond to the thiols: The sulfur atoms equally bind to two gold atoms and the ligands do not stand perpendicular on the surface. In the structure shown in Figure 1.5b ( $\text{Au}_{25}\text{SR}_{18}$  with  $\text{SR} = \text{phenylethanethiol}$ ), the 25 gold atoms are arranged in the following way: A central gold atom is surrounded by 12 other core gold atoms without bonds to a ligand. They constitute the vertices of an icosahedron, whose edges are colored in blue for visualization purposes. 12 of the 20 faces are capped centrally by a peripheral gold atom ( $12 + 12 + 1 = 25$ ). All peripheral gold atoms are bonded to 2 thiolate molecules, the gold atoms constituting the blue icosahedron only to one thiolate molecule ( $\frac{1}{2} \times [2 \times 12 + 1 \times 12] = 18$ ). Although



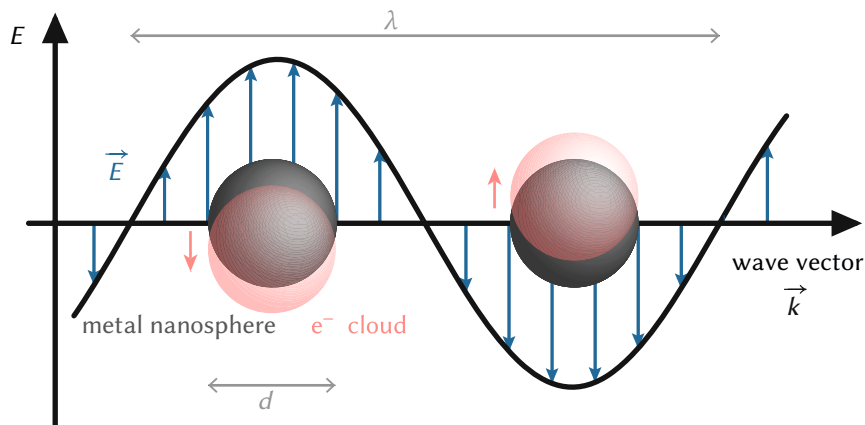
**Fig. 1.5:** The first two obtained crystal structures of thiolate-protected gold nanoclusters. a) SR = *para*-mercaptobenzoic acid, b) SR = phenylethanethiol. These illustrations were created with the software MERCURY 3.1.1 by the CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTRE using the crystallographic data provided by the authors of the referenced publications. Hydrogen atoms are omitted for clarity.

the gold–sulfur bonding mode might not be absolutely identical on the surface of larger gold nanocrystals, the structures shown here give a basic visual idea.

Although the gold–thiolate link is generally regarded as the most stable bond with gold surfaces, the bonding strength is still so low that it is known to be reversibly cleaved at temperatures over 60–80 °C.<sup>[262,263]</sup> Even at room temperature in organic solvents without an excess of thiols, the half-life of the bond is only about one day.<sup>[264]</sup>

**Optical properties of gold nanoparticles** The optical properties of AuNPs are a very important feature, since (i) optical spectroscopy is a powerful and convenient AuNP analysis method and (ii) most of the major AuNP applications are based on these special properties. Because the optical properties are directly related to the AuNP structure, gold nanoclusters and gold nanoparticles have different optical features. Both form very intensely colored colloidal solutions.

Gold nanoclusters exhibit molecular-like discrete electronic properties with single-electron transitions between quantized energy states at distinct wavelengths,

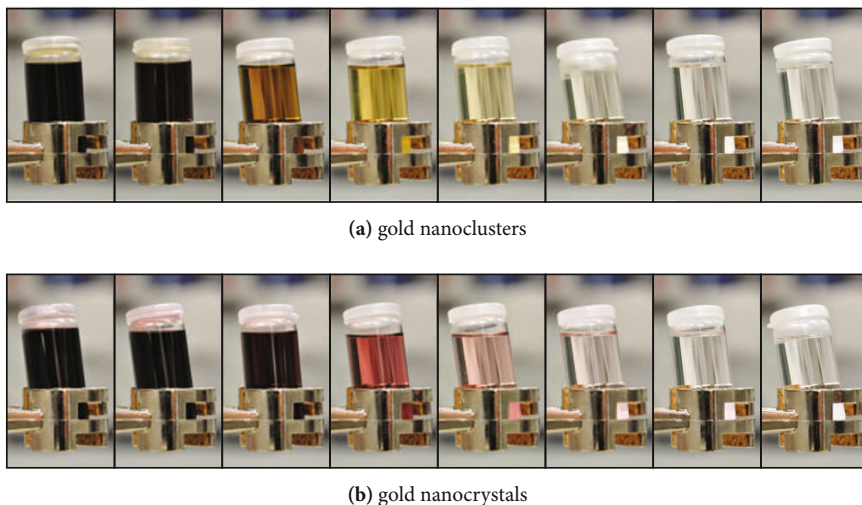


**Fig. 1.6:** Schematic illustration of the interaction of incident light with the confined conduction electrons of metal nanoparticles.

reminiscent of semiconductor quantum dots, at the lower end of the visible range.<sup>[265]</sup> The colloidal solutions are, depending on the gold concentration, dark brown or yellow. The photographs in Figure 1.7a show a colloidal solution of gold nanoclusters in methanol, which has been gradually diluted. In the case that only gold nanoclusters of a single size are present in the sol, distinct transition peaks can be seen in the optical spectrum.<sup>[266]</sup> Mostly, the nanoparticle sizes are distributed over a certain range and the signals overlap (see Figure 5.8 for an exemplary spectrum).

The optical excitations of crystalline AuNPs, on the contrary, are of a collective nature. The incident light excites the oscillation of conduction electrons against the restoring force of the positive gold nuclei,<sup>[267,268]</sup> as illustrated schematically in Figure 1.6 for a metal nanoparticle with the diameter  $d$ .  $E$  is the electric field strength,  $\lambda$  is the wavelength of the absorbed light. The effect is called *localized surface plasmon resonance*. (A plasmon is the quasiparticle corresponding to the quantized plasma oscillations.) The dependence on the wavelength of the incoming light is relatively weak, so that the plasmon resonance signal is relatively broad. In the case of gold nanospheres, it occurs at around 520 nm (see Figure 5.8 for an exemplary spectrum)—the colloidal solutions are vividly red. The photographs in Figure 1.7b show a colloidal solution of commercial gold nanospheres in methanol with increasing dilution.

The position and shape of the plasmon resonance peak is affected by the following factors:



**Fig. 1.7:** Photographs of gold nanosphere sols in methanol. The upper row shows gold nanoclusters (sample  $\text{Au}^{\text{Ibs}}\sqrt{\text{OH}}-6$ , see Section 5.1.3.2), the lower row shows gold nanocrystals (acquired commercially from ALDRICH). The concentrations are equal for photographs in the same column. From left to right they are:  $1.1 \text{ g mL}^{-1}$ ,  $0.37 \text{ g mL}^{-1}$ ,  $0.12 \text{ g mL}^{-1}$ ,  $41 \text{ mg L}^{-1}$ ,  $14 \text{ mg L}^{-1}$ ,  $4.6 \text{ mg L}^{-1}$ ,  $1.5 \text{ mg L}^{-1}$ , and  $0.76 \text{ mg L}^{-1}$ .

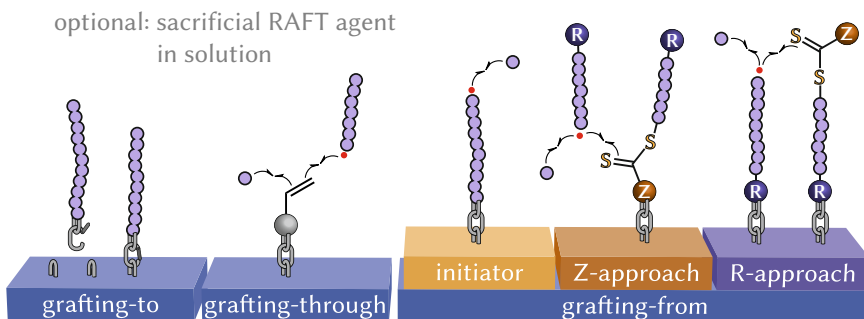
**Particle shape:** Non-spherical gold nanocrystals form colloidal solutions of completely different colors. Gold nanorods, for instance, exhibit two plasmon resonance peaks—a lateral and a transversal signal.<sup>[269,270]</sup> The following points refer mainly to spherical particles, as studied in this work.

**Particle size:** Larger particle sizes lead to a more pronounced plasmon resonance signal.<sup>[271]</sup> Up to a diameter of approximately 25 nm, the absorption band becomes narrower, after which it widens up again. The peak maximum is also shifted to longer wavelengths.<sup>[272]</sup> Hence, a more heterogeneous size distribution is reflected in a broader plasmon absorption peak.<sup>[273]</sup>

**Refractive index of the surrounding medium:** A high refractive index (or relative permittivity) of the solvent also shifts the peak to longer wavelengths.<sup>[267,268,274]</sup>

**Type of the ligands:** In addition to the ligands' effect on the refractive index around the AuNP, electron-withdrawing ligands lead to a similar effect as a smaller particle size.





**Scheme 1.5:** General synthesis strategies for the production of covalently bound polymer brushes using radical polymerization. The grafting-from approach is shown for the special case of RAFT polymerization. Z denotes the stabilizing group, R the re-initiating group in RAFT polymerization.

**Temperature:** A higher temperature leads to a slightly less pronounced plasmon signal.<sup>[273,275]</sup>

**Mutual approaching:** The plasmon modes are very sensitive to the interparticle distances. Mutual approaching to distances in the dimension of the resonance wavelength gives rise to additional resonances<sup>[276]</sup> at longer wavelengths—the effect of “plasmon coupling”.<sup>[277–279]</sup> The dispersion turns blue.

**Applications of AuNPs** Thanks to the dependence of the plasmon resonance signal on the interparticle distances, AuNPs hold great potential for (bio)sensing applications.<sup>[280–284]</sup>

Their manyfold medical applications<sup>[285,286]</sup> include the diagnosis of diseases,<sup>[287]</sup> photothermal anti-cancer therapy,<sup>[288,289]</sup> drug and gene delivery,<sup>[290]</sup> and the use as labels in electron microscopy “immunogold staining”<sup>[291]</sup> or contrast agents for computed tomography.<sup>[292]</sup> Some of these applications can be enabled by coating the AuNPs with polymers, in order to make them resistant to protein adsorption<sup>[293]</sup> and mask them from the body’s reticuloendothelial system.<sup>[294]</sup>

Other applications of AuNPs are catalysis,<sup>[295–299]</sup> surface-enhanced Raman scattering,<sup>[300,301]</sup> staining,<sup>[302]</sup> and their employment as compatibilizers in polymer blends.<sup>[303]</sup>

AuNPs are already widely used in industrial consumer products, such as cosmetics, food packaging, lubricants, beverages, automobiles, and toothpaste.<sup>[304,305]</sup>



### 1.2.4 Polymers on surfaces

A classic polymer coating—a traditional varnish—is applied on surfaces from solution in a quickly evaporating solvent or from a polymer melt. The varnish can be hardened by—typically UV-radiation induced—crosslinking. However, in all these conventional films, the polymer chains are only physisorbed, weakly attached by van-der-Waals forces, and lying flat on the surface. Only certain, hard, polymers can be used for such coatings. Furthermore, the polymer film is very thick, up to millimeters, which makes it impossible to reach the nanoscale with this approach.

In polymer brushes,<sup>[306–308]</sup> the macromolecular chains are linked to the surface through covalent bonds, formed by incorporated functional anchor groups.<sup>[309]</sup> The thickness of these brushes coincides with the length of the polymer chains and can therefore be fine-tuned with almost nanometer precision, enabling very fine surface patterning<sup>[310]</sup> and the coating of nanoparticles for the production of sophisticated nanohybrids. The coating of surfaces by polymer brushes with special properties can equip them with hydrophobicity,<sup>[311]</sup> protein repellence,<sup>[312,313]</sup> and antibacterial properties.<sup>[314]</sup> Also, parameters like roughness, biocompatibility, toughness, electrical conductivity, pH-compatibility, or heat resistivity can be specifically adjusted.<sup>[265,315–321]</sup>

Modern RDRP techniques (see Section 1.2.1.1) render it possible to employ radical polymerization for the production of covalently bound polymer brushes on surfaces. The three general synthesis strategies therefore are shown in Scheme 1.5:

**Grafting-to:** Preformed polymer chains with an incorporated functional group are grafted to the surface.<sup>[322]</sup> Such polymers can also be obtained from conventional radical polymerization using a radical initiator carrying the functionality.<sup>[323]</sup> Depending on the type of surface, it can be necessary to prefunctionalize it with complementary groups. Because of the steric hindrance entailed within the grafting-to strategy, it is difficult to achieve high grafting densities.<sup>[324]</sup>

**Grafting-through:** Molecules carrying unsaturated units are immobilized on the surface<sup>[325,326]</sup> and then built into the polymer chains propagating in solution.<sup>[327]</sup> This is by far the least used strategy of the three and does not necessarily rely on RDRP techniques either.

**Grafting-from:** The surface is first functionalized with a radical initiator<sup>[328,329]</sup> or an RDRP control agent,<sup>[330–332]</sup> so that the growing radical chains are directly bound to the surface at one end.<sup>[333,334]</sup> Here, a high extent of termination events can only be prevented when a mediating agent, rather than a radical initiator, is immobilized on the surface.

A typical group for anchoring molecules onto surfaces with hydroxyl groups (silica, quartz, aluminosilicates) is the trimethoxysilyl group.<sup>[335]</sup>

#### 1.2.4.1 RAFT polymerization from surfaces

Regarding the grafting-to approach to gold surfaces, a special feature of RAFT polymerization is that the active RAFT groups themselves are highly susceptible to chemisorption.<sup>[26,336]</sup> The RAFT group can therefore fulfill a second function after completion of the polymerization.

The grafting-from approach, in the case of RAFT polymerization, can be further subdivided into three fundamental strategies (see Scheme 1.5):

**Bound initiator:** This was historically the first performed approach. Only the radical initiator is tethered to the surface.<sup>[337–339]</sup> Although the RAFT agent in solution induces some control over the polymerization, in terms of control, this approach is clearly inferior to the other two. Note that the initiator-terminated polymer chains are usually neglected in an ideal RAFT polymerization (see Section 1.2.1.1).

**Z-approach:** The Z-approach is a unique feature of RAFT polymerization. Hereby, the RAFT agent is covalently bound to the surface with its stabilizing Z-group.<sup>[24,25]</sup> The radical chains propagate unattached in solution and return to the surface.\* With this approach, only living polymer will eventually reside on the surface—an ideal condition for the production of block copolymers.<sup>[340,341]</sup>

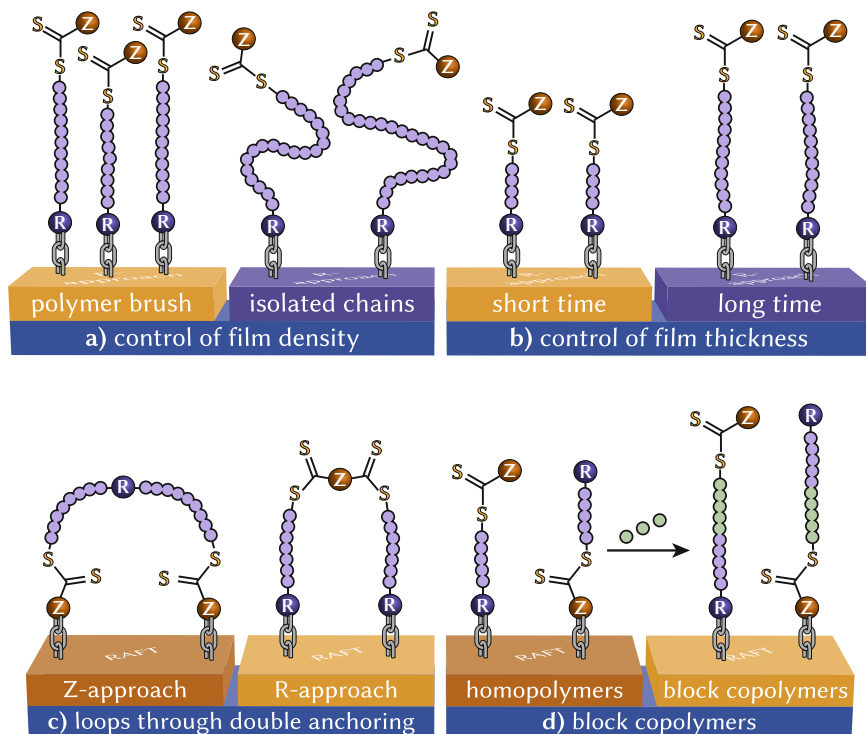
**R-approach:** The RAFT agent is covalently bound to the surface via a link at its R-group.<sup>[342–344]</sup> The polymer chains then grow from the surface and the RAFT end group is interchanged between the chains and remains accessible in the periphery.<sup>[345]</sup> Since even irreversibly terminated polymer chains will remain on the surface, a maximum grafting density can be achieved.

Even for the R- and the Z-approach, a so-called “sacrificial” RAFT agent is often added to the solution, in order to enhance the overall control.<sup>[346,347]</sup>

Scheme 1.6 gives an overview of the different methods of control that can be utilized in surface-confined RAFT polymerizations according to the grafting-from approach:

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\* Because of these characteristics, the Z-approach could also be regarded as a grafting-to technique.



**Scheme 1.6:** Ways of control in grafting-from surface polymerizations. Z denotes the stabilizing group, R the re-initiating group in RAFT polymerization.

**Scheme 1.6a: The grafting density** of the polymer can be adjusted prior to the polymerization by immobilizing the RAFT agents in the desired concentration. In the case of high grafting densities, a polymer brush is formed.<sup>[348]</sup> When the grafting density is lower, the polymer chains assume mushroom-like shapes.

**Scheme 1.6b: The thickness** of the polymer film increases linearly with the monomer conversion and can thus be specifically tuned.

**Scheme 1.6c: Polymer loops** can be created by anchoring both ends of a RAFT agent to the surface.<sup>[349–351]</sup> This can be done for the Z- (left) or the R-approach (right). Both halves of the RAFT agent remain connected to the

surface throughout the course of the polymerization. Due to steric hindrance, polymer loops cannot be produced with the grafting-to strategy.

**Scheme 1.6d: Block copolymers** on the surface can be formed via a sequential radical polymerization with another monomer.<sup>[352]</sup> If the order of monomer addition is dictated by their reactivity, both sequences are still accessible by using either the Z- or the R-approach.

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