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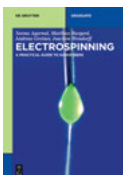**Twin Polymerization**

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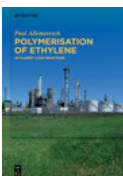Tadros, 2017
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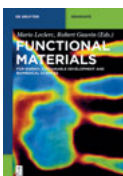ISBN 978-3-11-033180-6, e-ISBN 978-3-11-033351-0

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Twin Polymerization

New Strategy for Hybrid Materials Synthesis

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Preface

This book is the joint work of the scientists in the consortium of the DFG FOR 1497 (Research Unit of the Deutsche Forschungsgemeinschaft) with the topic: "Organic-Inorganic Nanocomposites through Twin Polymerization". The feature of twin polymerization is the targeted fabrication of inorganic/organic nanostructured hybrid materials by a simple procedure. The book is intended for material scientists and chemists with basic knowledge in organic chemistry and materials science. It describes the theoretical background, the physical chemistry and the combination of inorganic and organic chemistry of twin polymerization processes.

The book is structured into five main chapters: (1) Introduction, (2) Twin Polymerization – General Aspects, (3) Structure and Theory, (4) Materials, and (5) Applications.

The introduction generally explains polymerization reactions and various monomer structures. In this context, the classification of multifunctional monomers and complex polymerization cascades to hybrid materials are briefly discussed in comparison to common types of monomers and polymerization processes. Terms used for production of two polymers within one process, such as simultaneous polymerization and twin polymerization, are explained.

The variable synthetic concept of twin polymerization for the production of manifold molecular structure combinations in hybrid materials is introduced in Chapter 2. Also, various methodologies for the production of polymer organic/inorganic hybrid materials compared to twin polymerization are presented. The different types of twin polymerization and related processes are classified according to established IUPAC nomenclature. The differentiations and similarities of aspects of twin polymerization compared to simultaneous polymerization and other types of multifunctional monomer polymerizations are discussed in detail.

Twin polymerization is determined by the chemistry of a new class of monomers, so-called twin monomers, which are the topic of Chapter 3. The versatility of possible twin monomer molecule structures is addressed by structure investigations and quantum chemical calculations in subchapters of that chapter. Therefore, the structure–reactivity relationships of various twin monomers as functions of elemental compositions are demonstrated in detail. The general classes of precursors being suitable for twin polymerization and their specific structural features are presented in Chapter 3.1. The relationships between their structural features and their reactivity in the polymerization process are discussed. In addition, the influence of the chemical nature of the precursors with regard to the properties of the as-obtained polymerization products, e.g., organic/inorganic nanocomposites, is unveiled.

The fourth chapter describes the production of various nanostructured hybrid materials which are available by twin polymerization. Silicon-related and inorganic oxide hybrid materials, carbon materials and metal nanoparticles within hybrid materials are addressed in subchapters. Chapter 4.1 describes which types of twin

monomers are suitable to produce nanostructured silica and silicon nitride-related polymer hybrid materials. A special aspect is the characterization of the molecular composition of hybrid materials by solid state NMR spectroscopy and morphology investigations by various electron microscopy techniques. The application of the simultaneous twin polymerization by use of functional twin monomers for the fabrication of tailor-made ternary siliceous hybrid materials is particularly emphasized. Carbon materials derived from nanostructured hybrid materials of twin polymerization processes are the content of Chapter 4.2. In Chapter 4.3, the variety of porous inorganic oxides and mixtures of porous inorganic oxides that have been obtained using the concept of twin polymerization so far are presented. The different concepts for their synthesis exploiting distinguishable polymerization protocols are explained. The chapter closes with an overview of potential applications for these porous oxide materials. The twin polymerization of diverse main group and transition metal-containing twin monomers and metal carboxylates as well as tin alkoxides as a source for metal and metal oxide nanoparticles to produce porous carbon and silica hybrid materials, respectively, decorated with metal or metal oxide nanoparticles or tin alloys is discussed in Chapter 4.4. In addition, the encapsulation of metal and metal oxide nanoparticles within porous carbon shells by using twin polymerization is reported. Current trends in this field of chemistry are discussed as well.

In Chapter 5, applications of twin polymerization are compiled. Chapter 5.1 shows the application of carbon-containing materials as electrode materials for rechargeable lithium-ion batteries synthesized over the concept of twin polymerization. Electrochemical tests of anode materials based on germanium (Ge@C), tin ($Sn@SiO_2/C$), and tin alloys ($Sn_xM_y@SiO_2/C$; M = Co, Ni, Sb) as well as cathode materials based on sulfur-containing carbon hollow spheres are presented. A comparison with literature state of the art materials and values is given. Combination of various twin monomers with each other and/or with conventional monomers for polymerization is a suitable tool for the production of various hybrid material compositions on demand by a modular concept. The specific application of twin polymerization in combination with other polymer syntheses, such as polyepoxides and polyurethanes, is covered in Chapter 5.2.

Concluding remarks emphasize the perspectives of the twin polymerization process for the development of new hybrid materials as inspiring concept in materials science.

Contents

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1 Introduction

Polymerization reactions are of great importance for the fabrication of a variety of plastics, resins, composites, and rubberlike materials [1–7]. Hence, a variety of polymerization reactions and related processes have been developed for materials syntheses and related purposes over the last decades. Regardless of the mechanism of polymerization, the molecular structure of a polymer (and hence its properties) is also determined by the functionality and molecular composition of the monomers.

Furthermore, in polymerization reactions, organic monomers are often used in combination with diverse types of solid materials, such as metals, ceramics, and inorganic oxides, to fabricate hybrid and composite materials [8–12]. Hybrid materials are advantageous for many applications because they combine the properties of plastics, resins, and rubbers with those of solid inorganic materials in a synergistic manner. Presentations of concepts for hybrid material production are the main objective and motivation of this chapter. For this purpose, a novel polymerization principle is implemented.

Polymeric organic/inorganic hybrid materials consist of two or more solid components whose properties are determined by chemical composition, morphology, and topology of the interfaces. The ratio of the atoms at the surface corresponds approximately to that of the volume units of the components. Therefore, for hybrid materials, the domains of the individual components must be on a length scale of a few nanometers [8–10]. Thus, genuine hybrid materials show chemical and physical properties which are different from those of the individual components. That is the striking difference to traditional composite materials in which the characteristics are determined by the individual component but purposefully modified by the second component.

The key point in hybrid materials synthesis is that two different polymeric components must be simultaneously synthesized. For the production of nanostructured organic/inorganic hybrid materials, it is of importance that both polymers simultaneously develop within one overall polymerization process. That is a challenge when two polymerizable groups of two different monomer species are employed which are different in their kinetic behavior. The even arrangement of nanostructure only results when the originating polymer strands remain in vicinity to each other. In other words, phase separation of the two differently formed polymer components does not take place. This feature can be realized by the use of specifically constructed monomers or by polymerization techniques for the hybrid materials synthesis. The inorganic component of hybrid materials can be of a different nature, such as inorganic oxides, metal particles, or carbon allotropes. Organic polymers usually are polyolefins, polyesters, polyamides, and resins. Organic polymer syntheses by step-growth or chain polymerization are widely employed. Mostly, the sol-gel process is used for oxidic components, whereas metals and carbon materials are obtained by post-reactions of hybrid materials such as chemical reduction processes or thermal treatment. The

sol-gel process is a step-growth polymerization, which is not specifically addressed in this book, whereas other relating processes are considered.

The fundamentally different polymerization mechanisms leading to inorganic and organic polymers are discussed in Section 1.1.

Classification of hybrid materials is not trivial because various aspects play a role. Classification may include the composition, synthetic methodology, or kind of interaction of the targeted components. In literature, the type of interaction of the components has been accepted as prime criterion to classify a hybrid material [13–22].

Siliceous components play an important role in hybrid materials synthesis which is also an extensive part in this monography. For a better understanding, silica hybrid materials will be briefly used as instructive example to explain the nomenclature of hybrid materials.

To explain the conception of this book, we will demonstrate that the polymerization process of each monomer is decisively determined by its functionality, especially the number of functionalities. Functionality f means how many bonds the monomer can form to other partners or to itself (see Fig. 1.1). Molecules with $f=1$ are unsuitable for polymerization. For the case $f=2$, a linear chain or cycle results. Monomers with $f=3$ can deliver various polymer structures depending on reaction conditions and chemical composition of the monomer. Thus, trialkoxysilanes [R–Si(OR)$_3$] ($f=3$) can react in different ways under formation of polymeric silsesquioxanes or cubic silsesquioxanes [8, 11].
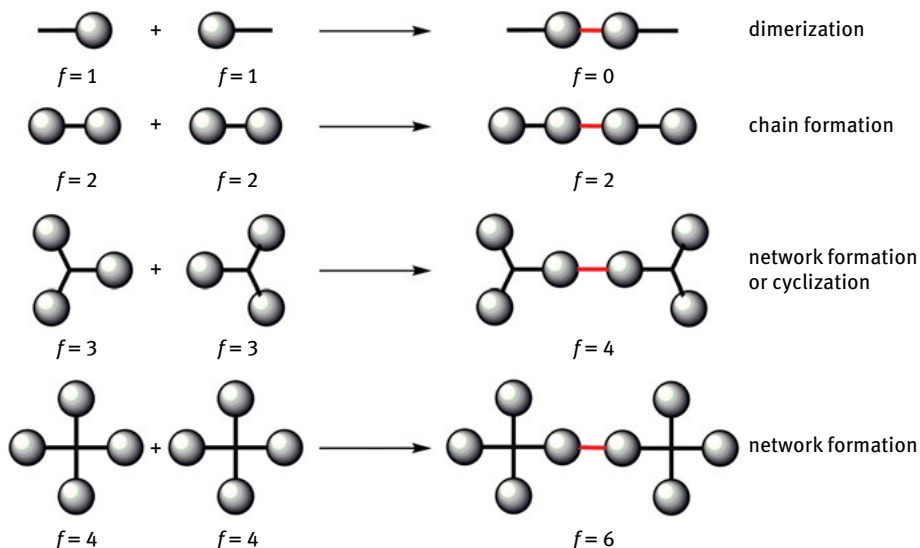
Fig. 1.1: Functionality of hypothetical reactant molecules and resulting functionality of the product. Each spherical part of each reactant is able to form one new bond to another sphere. The new bond formed is red marked in each product. The product of dimerization might result from addition or condensation reaction. Condensation by-products are not shown for clarity.

The case $f = 4$ is typical for silica network formation. The situation becomes more complex when monomer mixtures or multifunctional monomers are employed. But in principle, the concept of functionality remains valid.

In case that one generated component rapidly undergoes crosslinking, i.e., silica formation among the sol-gel process, simultaneously formed (linear) polymer strands can be physically entrapped and thus do not migrate. Those types of hybrid materials, containing one of the components physically bonded, are classified as type A (Mackenzie) or Class I (Sanchez) hybrid materials [13–17]. With regard to the synthesis, it is of importance for this type of hybrid materials to note that so far, two completely different polymerization processes, one for each component, were used within one procedure. For the production of this class of hybrid materials, the combination of two simultaneous polymerizations (SPs) of two common, but structurally different, monomers is suitable.

Mackenzie also introduced type B hybrid materials, which are characterized by forming strong hydrogen bonds between the components, but there is no covalent bond. If the two different polymeric components are covalently bonded within the hybrid material, they are classified as type C (Mackenzie) and Class II (Sanchez), respectively. The classification of hybrid materials with respect to the kind of interaction is illustrated in Figure 1.2. The blue points in the left drawing represent physically entrapped molecules. The yellow and orange sections are crosslinked inorganic or organic polymers.

For the production of Type C or Class II hybrid materials, the use of special so-called heterobifunctional monomers is required. They contain two structurally
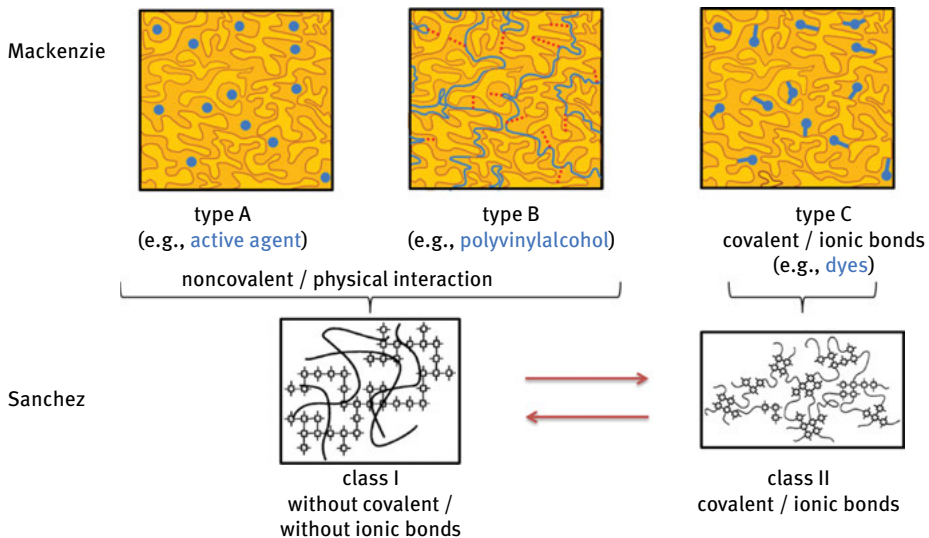
Fig. 1.2: Accepted nomenclature of hybrid materials with respect to the kind of interaction of the components according to Mackenzie and Sanchez [13–17].

different groups which can polymerize independently of each other. The different groups are connected to each other by strong covalent bonds which are not easily cleavable. The importance of both monomer design and functionality for hybrid material fabrication is set out in detail in the second part of the introduction.

To gain a better understanding of the types of polymerization reactions established in relation to the topic of this book, the classification of polymerization reactions will be briefly explained. For a more profound lesson on special aspects, the reader should revert to the references given in each chapter. In the second part of the introduction, the content is focused on different types of monomers and their functionalities because the main topic of this book deals with novel monomer architectures for the production of hybrid materials. In the third part, this introduction focuses on established and novel specifically designed monomers which are suitable to produce organic/inorganic hybrid materials within one integrated process. The two different types of complex monomers are explained with respect to functionality of the respective monomer fragment suitable for chain or step-growth polymerization. The special features of twin monomers are discussed.

1.1 Polymerization mechanisms

Polymerization reactions are very complex and several types of polymerization reactions are known. However, polymers are formed following two main mechanisms. These are step-growth polymerization and chain polymerization [1, 2, 7]. These modern classifications of polymerization types have been finally accepted, compared to the conventional perception originally introduced by *Carothers* [5, 6], because the kinetics of each of the reaction cascades are completely different [1, 2, 7]. Each polymerization reaction can be attributed to one of these basic mechanisms.

Step-reaction polymerizations (or step-growth polymerizations) are characterized by the random arrangement of monomers which can form dimers, trimers, tetramers, and longer molecular chains. In case of linear step-growth, the functionality f is at least two in both the growing polymer and the monomer. Each of the reactive monomers and intermediate products among the step-growth process contains functional groups that react with each other. Thus, dimeric chain-lengthening fragments and starting monomers can react spontaneously with each other to form macromolecules using about the same activation energy for each crucial growth step. The rate of a step-growth reaction can be increased significantly by applying an appropriate catalyst. In textbooks, these functional groups are mostly denoted as A and B [7].

Two types of monomers for step-growth polymerization are known: A–B-type monomers and a combination of A–A with B–B monomers. This established concept only considers the reaction of A with B. In practice, particular A–A-type monomers (or B–B) can also readily undergo step-growth polymerization. It depends on the

chemical composition whether A–A or B–B monomers can polymerize spontaneously. Condensation polymerization of A–A monomers is important for producing inorganic polymers and networks because silanol groups, for example, actually react to siloxane moieties and water at ambient temperature. Likewise, methanediol (the hydrate of formaldehyde) spontaneously polymerizes to paraformaldehyde in water solution. Consequently, the polymer strands, instantaneously formed from such A–A monomers, undergo further condensation which makes their storage difficult. Usually, reactive A–A monomers are generated *in situ* by hydrolysis of the corresponding precursors, e.g., dialkoxysilane compounds, or by dissolution of formaldehyde in aqueous solution. However, dicarboxylic acids and diols also belong to the class of A–A or B–B monomers but are less reactive. In principle, dicarboxylic acids can react toward polycarboxylic anhydrides and diols to polyethers, but compared to the actual running polyester, these chemical reactions are not preferred.

Similar to readily polymerizable A–A monomers, shelf-life and storage conditions of A–B monomers are determined by the activation energy of the elementary step. Hence, for polyester synthesis, the A–B monomers are frequently generated *in situ* by ring-opening of lactones with traces of water. Otherwise, potential A–B monomers such as pure amino acids behave inertly due to their betaine structure. In this case, the ring-opening of lactams with a low portion of water is useful to generate the A–B monomer as intermediate during polymerization.

Often, step-growth polymerization of less reactive A–B monomers can only be induced by a catalyst. For instance, *p*-bromostyrene can be catalytically polymerized by step-growth to *p*-poly(phenylenevinylene), which is known as the Heck reaction. Furthermore, there are also particular step-growth polymerization processes, which essentially require both a catalyst and an additional reactant (oxidizing agent), i.e., the synthesis of poly(oxy-2,6-dimethyl-1,4-phenylene) from 2,6-dimethylphenol. In this category, production of several conjugated polymers, such as polyaniline and polythiophene, has to be considered as well [1].

Hypothetically, each organic molecule can serve as A–B monomer for step-growth polymerization. Hence, ethylene can theoretically polymerize to polyacetylene and dihydrogen. But this reaction does not take place. The reaction is neither thermodynamically favored nor does a suitable catalyst exist. Please remember that a thermodynamically favored reaction requires $\Delta_R G^{\ominus}$ to be negative at a given reaction temperature (Eq. 1).

$$\Delta_R G^{\ominus} = \Delta_R H^{\ominus} - T \Delta_R S^{\ominus} \tag{1}$$

Scenario $\Delta_R G^{\ominus} < 0$ is fulfilled, if $\Delta_R H^{\ominus}$ is negative and its contribution is stronger than that of the entropy term $T \Delta_R S^{\ominus}$. $\Delta_R S^{\ominus}$ for polymerization reactions are mostly negative excluding specific ring-opening polymerizations (ROPs) such as that of sulfur [11]. Further reading about thermodynamics of polymerizations is referred to textbooks for polymer chemistry [18, 19].

The combination of A–A with B–B monomers is the most used methodology for production of step-growth polymers because the reaction starts only when the monomer mixture (A–A + B–B) is prepared. Representative examples for step-growth polymerization reactions are shown in Scheme 1.1.

A–A type of polymerization
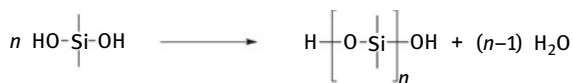
A–B type of polymerization
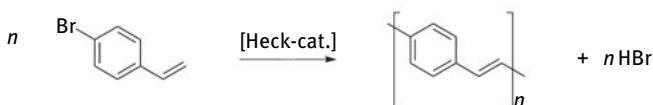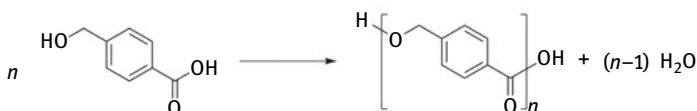
A–B + B–B type of polymerization
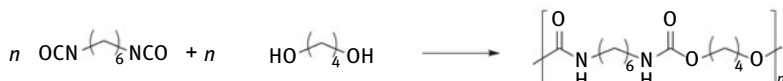
Scheme 1.1: Different types of step-growth polymerization processes to form linear polymers.

The dependence of the degree of polymerization DP_n as a function of the monomer conversion is an important relationship in polymer synthesis. The average degree of polymerization DP_n is defined as the number of monomer units in one macromolecule (Eq. 2):

$$DP_n = \frac{M_n}{M} \tag{2}$$

M_n is the number average molecular weight of the polymer and M the molecular weight of the starting monomer. The relationship between DP_n and overall conversion (p) of the functional monomer groups of step-growth processes can mathematically be expressed by the well-established *Carothers* equation (Eq. 3) [1, 2, 7].

$$DP_n = \frac{1}{1-p} \tag{3}$$

From Equation 3, it can be derived that nearly complete conversion is necessary to achieve a high DP_n. An important issue of step-growth polymerizations is that the polymerization rate steadily decreases with increasing conversion of functional groups due to their self-dilution. Importantly, Equation 2 is only fully valid for linear chain formations with $f = 2$. Cyclization reactions are not taken into consideration by Equation 2. The calculation of the proportion of cyclization reaction among linear polymer chain formation requires the use of a modified *Carothers* equation. This feature is explicated in special textbooks [4, 20].

For step-growth polymerization, monomers and monomer combinations with an average functionality higher than two as well as mixtures of monomers with different functionalities can be used. Then, the average functionality (f_{av}) must be taken into account. In case that f_{av} of monomers ($A_x B_y$, $x,y > 2$) is greater than two, crosslinking between growing chains might occur. Then, the extended *Carothers* equation (Eq. 4) allows the determination of conversion of the theoretical gel point at which an infinite polymer network ($DP_n \rightarrow \infty$) is formed ($p \approx 2/f_{av}$).

$$DP_n = \frac{2}{2 - f_{av} \cdot p} \tag{4}$$

$f_{av} = (xn + ym)/(n + m)$; x and y are the stoichiometric factors of functionality of the monomers with respect to A and B, n and m are the molar portions of the monomers A and B, respectively, in the polymerization mixture. For instance, if the stoichiometric factors f (or $x = f_A$ respectively $y = f_B$) for a common A–B monomer ($n = m = 1$) are both one, then it follows $f_{av} = 2$.

Network formation is already possible without complete conversion of functional groups if $f_{av} > 2$. Silica formation from tetraalkoxysilane [$Si(OR)_4$] in the sol-gel process is a typical network formation with $f = 4$ because the *ortho*-silicic acid [$Si(OH)_4$], which is considered as theoretical model, can be assumed as a monomer of an A_4-type. Then, $\geq 50\ \%$ conversion of Si–OR groups is theoretically sufficient for network formation to take place. Tetraethoxysilane, $Si(OC_2H_5)_4$, is the most frequently used precursor monomer for silica fabrication in sol-gel processing [21–23].

The active species directly suitable for step-growth polymerization, the Si–OH functional group, is only formed when $Si(OC_2H_5)_4$ reacts with water in an upstream reaction. This aspect must be considered for all types of M–O–alkyl species (M = Si, B, Ti, Sn, etc.) when used in hybrid materials synthesis.

Step-growth polymerization of AB_m monomers (f for A is 1, $m = 2, 3, 4, ...$) can yield branched polymers, yet only if both A and B cannot react with themselves (see Refs. [21, 24]).

Chain-reaction polymerizations do not start spontaneously at ambient temperature in contrast to common step-growth polymerizations. An initiator is necessary to induce the chain polymerization reaction. The most important monomer species for chain polymerization reactions are ethylene derivatives, mainly 1-olefins. Such

ethylene-based monomers are often called vinyl monomers. Polymerization of olefins and several kinds of ROPs belong to the class of chain polymerization. Typical examples for chain polymerizations are demonstrated in Scheme 1.2.
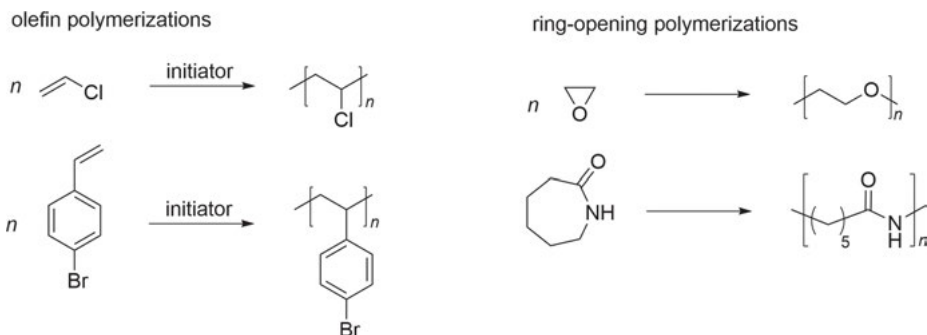
Scheme 1.2: Important types of chain-addition polymerizations. Each reaction equation illustrates only the gross propagation reaction. Compared with Scheme 1.1 (A–B type of polymerization), *p*-bromostyrene as monomer can form two different polymers, depending on whether a Heck catalyst or radical initiator is used.

The functionality of two ($f = 2$) of an olefin results from the double bond, which can form two σ bonds toward two other molecular fragments in a typical addition reaction as known from organic chemistry. In case olefins react with each other, a linear chain results.

For a better understanding in comparison to the step-growth polymerization, it might be assumed that a growing, active chain end with DP_n* has a functionality of one. After addition of one monomer with $f = 2$, the functionality of the DP_{n+1}* active growing chain end remains one (Scheme 1.3). Thus, f is one in an individual growing polymer chain but its value is two in the monomer. That is contrary to step-growth polymerization, where both are two. Therefore, *Carothers* equation cannot be applied to chain polymerization.

Scheme 1.3: Number of functionalities of a growing active polymer chain (f_{CP}*) and corresponding monomer.

However, the situation for chain polymerization is more complex. A chain-reaction polymerization involves different individual chemical processes: initiation, propagation, termination, and transfer reactions. Each of these distinct reactions is different concerning the elementary chemical processes. Furthermore, there are four main

initiation reactions of chain polymerizations to consider: radical, cationic, anionic, and transition metal complex coordination (i.e., Ziegler–Natta polymerization, metallocene polymerization, metathesis polymerization). The initiation, propagation, transfer, and termination reactions of each individual chain polymerization either radical, cationic, or anionic are completely different. Therefore, it is impossible to consider all known chain polymerization reactions in a universally accepted kinetic scheme.

There are several common aspects which can be discussed basically for chain-addition polymerization reactions. In principle, the average degree of polymerization DP_n of chain polymerization reactions is a function of both monomer $[M]$ and initiator concentration $[I]$ [1, 2, 4, 7]. The mathematical expression DP_n as a function of $[M]$ and $[I]$ is different for free radical polymerization (FRP), controlled radical polymerization, cationic polymerization, anionic polymerization, and transition metal-catalyzed polymerization. The reason for this fact is that DP_n as a function of monomer conversion ($d[M]/dt$) and initiator concentration depends on many factors which are determined by the detailed mechanism of polymerization. Often, the concentration of the active initiator is determined by complex equilibria of the reactants. Furthermore, DP_n depends on the extent to which transfer and termination reactions play a role. Notably, termination reactions of FRPs and ionic polymerizations are completely different in their nature, because radicals can annihilate each other, whereas equally charged chains do repel. The situation is still more entangled if ionic aggregates are involved.

Generally, DP_n (Eq. 5) is approximately the rate of propagation (v_p) divided by the sum of both rates of termination (v_t) and transfer reaction (v_{tr}).

$$DP_n \approx \frac{v_p}{v_t + v_{tr}} \tag{5}$$

In FRP, long chains are formed from the beginning of the reaction because propagation reaction (v_p) occurs much faster than initiation (v_i). Thus, the conversion of monomer has no great influence on average molecular weight.

Living chain polymerizations are characterized as those in which neither transfer nor termination reactions take place. That is $v_i \gg v_p$ and $v_t + v_{tr} = 0$. In living polymerization, average degree of polymerization increases linearly with conversion of the monomer (Fig. 1.3). In this case, DP_n at complete monomer conversion can be simply calculated by Equation 6. $[M]$ is the initial concentration of monomer and $[I]$ the real concentration of initiator.

$$DP_n = \frac{[M]}{[I]} \tag{6}$$

Equation 6 can only be applied when v_i is greater than v_p. That condition can be accomplished for several anionic and cationic polymerization reactions of olefins and cyclic compounds [25, 26].

Examples of Scheme 1.2 are selected according to the aspect that the propagation reaction delivers a structurally well-defined polymer with regioselectively linked
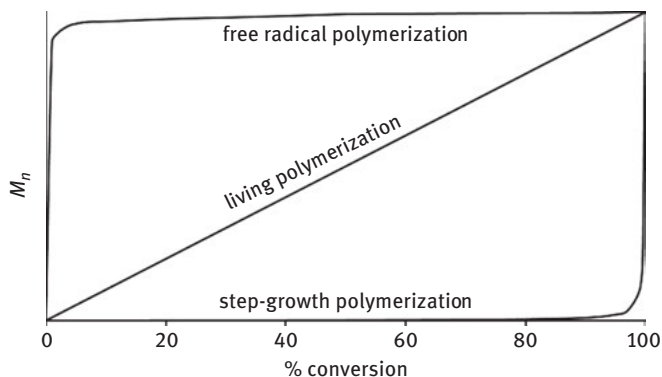
Fig. 1.3: Molecular weight M_n or degree of polymerization DP_n as a function of conversion of functional groups for free radical, living, and step-growth polymerization.

monomer units. That is not always the case. In other cases where an olefin monomer can particularly undergo isomerization reactions during polymerization, the resulting polymer constitution (structure) is often difficult to describe. The representative example for this occurrence is buta-1,3-diene polymerization, which can produce a mixture of different constitutional and configurational isomers along the same polymer backbone and between different polymer strands. That feature has to be considered independently of the mechanism of buta-1,3-diene and related to, i.e., isoprene polymerization. Altogether, 1,4-*cis*, 1,4-*trans*, 1,2-*isotactic*, 1,2-*syndiotactic*, and 1,2-*atactic* repeating units are theoretically possible. Thus, the sole term polybutadiene is not sufficient to describe the exact structure. Principally, "polybutadiene" isomers along the chain can also be classified as copolymer resulting from "1,2-butadiene" and "1,4-butadiene." But this description is not used. Commonly, the composition of each specific polymer sample is given as extra information.

ROPs show some peculiarities which are determined by the nature of the monomer and the mechanisms of polymerization. There are two types of ROP, that of cyclic compounds which contain breakable σ bonds or π bonds. The latter do polymerize by the ring-opening metathesis polymerization (ROMP) which will be discussed subsequently.

The functionality of two ($f = 2$) of a cyclic compound such as ethylene oxide or ε-caprolactam results from the breaking of a σ bond. The breaking of a σ bond in a cyclic compound provides two reactive sites ($f = 2$) which can form a chain (e.g., see Scheme 1.2). These basic considerations are independent of the polymerization mechanism.

The mechanism of addition-ring-opening polymerization of monomers is clearly a chain growth in the case that the active species is attached to the active polymer chain. For ROP, which occurs by activated monomer ring-opening mechanism, the situation is more complex [27]. Principally, nearly each polymer which can be produced

by ROP can be alternatively synthesized by a condensation polymerization. Therefore, specific ROPs must be handled with care regarding their classification. But a distinction between chain- or step-growth mechanisms is always possible.

ROMP of cyclic olefins is also a chain polymerization of which the course is strongly dependent on the nature of catalyst used. Living ROMP has been established as a valuable tool for the production of tailor-made polymers [28]. The polymerization of acyclic olefins and di-olefins with a metathesis catalyst requires special attention because interference of chain-growth and step-growth reaction is possible as a function of monomer structure and resulting polymer [28–30]. The functionality of a monomer suitable for metathesis polymerization is two, as well, but with regard to both σ and π bond of the double bond, which can form only one double bond during polymerization.

Thus, in contrast to ROMP, the polymerization of nonconjugated, linear dienes (**a**cyclic **d**iene **met**athesis, ADMET) takes place by the use of identical catalyst and similar mechanism on the molecular level. But it requires a special consideration because in that case genuine step-growth polymerization takes place which is connected with ethylene (or ethylene derivative) elimination [30]. Thus, in olefin metathesis polymerization, the molecular structure of the monomer determines the polymerization process rather than the catalyst. This example is completely in contrast to the *p*-bromostyrene monomer example where the initiator or catalyst determines the course of polymerization and product formation (see Schemes 1.1 and 1.2). That comparison will show that any decision whether chain or step-growth polymerization takes place should be carefully reviewed.

Polymerization of monomer combinations

Molecular composition of polymers can be adjusted in a wide range by using the **copolymerization** techniques. Copolymerization is useful for both step-growth and chain polymerization. Copolymerization is a valuable tool for tailoring properties of industrial chain polymers. These aspects are the content of many established polymer chemistry textbooks [1–4]. There are different possible scenarios when two monomers are polymerized together within one procedure. Statistical copolymerization, alternating copolymerization, block copolymer formation, and SP can take place (Scheme 1.4).

Apart from the formation of copolymers, when two different monomers are chain polymerized within one composition, the formation of two homopolymers can also take place. This scenario is usually not specifically treated in polymer text books because it is undesirable in practice for chain polymerization. Another extreme scenario is the so-called selective polymerization. In this case, only one of the monomers (M_1) undergoes polymerization and monomer M_2 remains unaffected. That behavior is observed for anionic or cationic chain polymerizations of monomers which differ significantly in their reactivity. This procedure may be suitable for special application if M_2 can be used in a consecutive step to form a second polymer component.

$$m\,M_1\ +\ n\,M_2$$

$\sim\!\sim M_1\text{-}M_2\text{-}M_1\text{-}M_1\text{-}M_2\text{-}M_2\text{-}M_2\text{-}M_1\sim\!\sim$ statistical copolymerization

Poly(M$_1$-*stat*-M$_2$)

$\sim\!\sim M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1\text{-}M_2\sim\!\sim$ alternating copolymerization

Poly(M$_1$-*alt*-M$_2$)

$[M_1]_m$-$[M_2]_n$ block copolymerization

Poly(M$_1$)-*block*-Poly(M$_2$)

$[M_1]_m\ +\ [M_2]_n$ simultaneous polymerization

Poly(M$_1$)   Poly(M$_2$)

$[M_1]_m\ +\ n\,M_2$ selective polymerization of M$_1$

Poly(M$_1$) $n\,M_2$
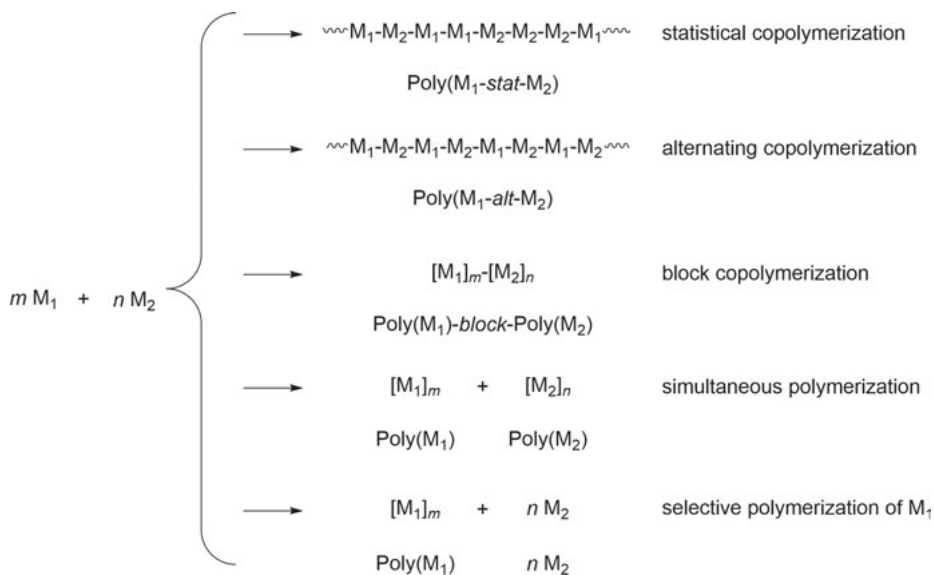
Scheme 1.4: Possible scenarios when two monomers are mixed together and then polymerization is started within one chemical process.

Let us now consider the scenario when two monomers do simultaneously polymerize but cannot copolymerize. SP of two monomers within one procedure is a suitable methodology to produce polymer blends or organic/inorganic hybrid materials. From the above arguments, the conclusion follows that DP_n as a function of conversion of monomer is completely different for FRP, step-growth, and living chain polymerization, which is illustrated in Figure 1.3.

Especially, DP_n versus conversion behavior of FRP is contrary to step-growth polymerization (see Fig. 1.3). High molecular weight polymers are obtained due to the very fast propagation speed of FRP already at low monomer conversion. The situation for step-growth polymerization is derivable from Equation 3 showing that a high degree of polymerization is only possible at high p.

To develop a material consisting of two different polymers requires a synthetic protocol where the two different polymer structures are generated simultaneously within the overall process. Therefore, combination of either two different chain or two different step-growth polymerizations is, as expected, advantageous in that both polymerizations are similarly fast and DP_n increases in a similar way. Therefore, combination of FRP with step-growth polymerization for the production of hybrid materials is expected to produce inhomogeneous hybrid materials due to the different time scales of the individual polymerization rates. This point is of great importance for discussing aspects of the SP.

That feature is hard to realize when only chain polymerizations of olefins are employed because often copolymers are formed or one monomer does not react

and thus polymer/monomer mixtures result (see Scheme 1.4). Combination of chain polymerizations to produce hybrid materials is still a challenge. Only simultaneous chain polymerization of acrylate monomers together with epoxide monomers as a concrete beneficial example has been reported in literature. The acrylate monomer polymerizes by a radical mechanism and the epoxide by a cationic polymerization. Both active growing chain ends do not evidently interfere with each other. Thus, a polymer/polymer hybrid material of polyacrylate/polyepoxide is formed (Scheme 1.5) [31–33]. The advantage of this process is that two different chain polymerizations, olefin polymerization and ROP, can be beneficially combined.
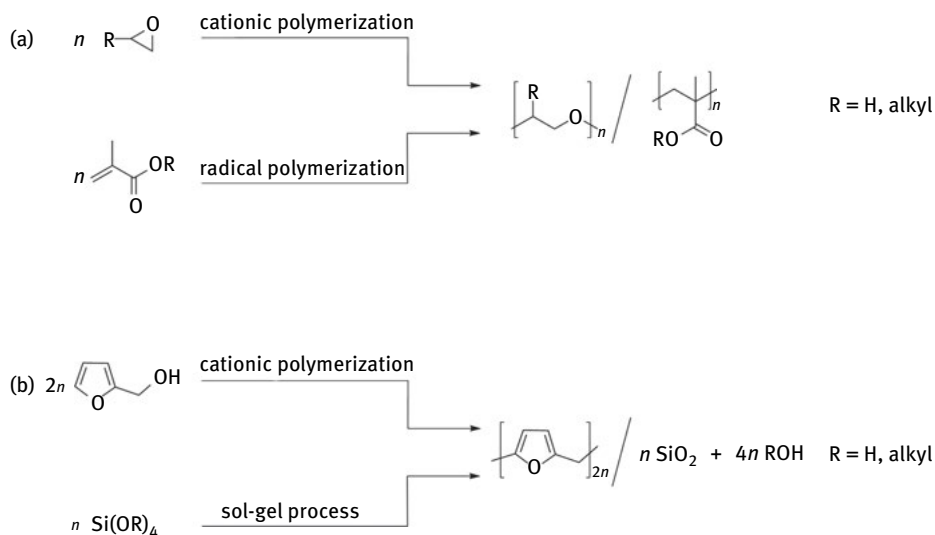
Scheme 1.5: Two established examples of simultaneous polymerizations for fabrication of hybrid materials. (a) Synthesis of interpenetrating polyepoxide/polyacrylate hybrid material by combination of two chain polymerizations. (b) Synthesis of a polyfurfuryl alcohol/silica hybrid material by combination of two step-growth polymerizations.

In contrast to SP of chain polymerizations, simultaneous step-growth polymerization processes are widely used for the production of organic/inorganic hybrid materials because the sol-gel process of silicon- and metal alkoxides belongs to the category of step-growth processes [21–23, 34]. For instance, combination of sol-gel chemistry and step-growth polymerization of furfuryl alcohol has often been used to fabricate polymer/silica hybrid materials [35, 36]. SP techniques will be discussed again as an alternative route compared to twin polymerization in Chapter 2.

The examples of SP to produce hybrid materials as demonstrated in Scheme 1.5 are particularly advantageous for the reason that two polymerization processes are combined which are even adapted in their kinetics.

The conception of polymeric hybrid materials synthesis requires the consideration of various polymers achievable from either step-growth or chain polymerization

reactions. As mentioned before [1, 2, 7], step-growth polymerization, (free radical) chain polymerization, and "living" polymerization are totally different with regard to DP_n as a function of conversion of functional groups (see Fig. 1.3). Thus, their SPs to high molecular weight polymers are limited.

Principally, the drawback can be overcome if the functional group is both step-growth and chain polymerizable. There are only few chemically reactive groups which can undergo both chain and step-growth polymerization. Isocyanates and epoxides belong to this class of monomers. Formaldehyde is a special monomer molecule which can undergo chain polymerization and serve as component in step-growth polymerization due to its high carbonyl reactivity. Related carbonyl compounds (aldehydes and ketones) can also theoretically operate in this way, but their reactivity strongly decreases with increasing π-bonding energy of the carbonyl bond. Therefore, the combination of the chemical reaction of groups which are suitable for chain and step-growth polymerization may be advantageous to assemble both polymerization processes. That feature can be realized when two polymerizable groups are integrated within one molecule. These are multifunctional monomers. Their occurrence in the course of polymerization will be discussed in the next section.

1.2 Characteristics of multifunctional monomers

In polymer chemistry, multifunctional monomers are defined as molecule compounds that contain more than one polymerizable group with $f = 2$. There are two types of multifunctional monomers depending on whether the bond connecting the two polymerizable groups is cleavable or persists during the chemical processing. Cleavable monomers commonly react with water or other reagents at ambient temperature. This process results in two different monomers which can polymerize by different mechanisms (see Section 1.3).

The discussion starts with a class of compounds that have a not easily cleavable bond. Amide or ester groups are suitable for this purpose linking the polymerizing groups. The simplest case is a bifunctional monomer, e.g., bisacrylate, where two vinyl monomer units are covalently linked together *via* a spacer. Then, the overall functionality is four. In the case of the chemical structure of diverse polymerizable groups being identical in one molecule, the monomer should be classified as homo-*N*-functional. *N* denotes the number of identical functional groups. $N = 2$ corresponds to a homobifunctional monomer ($f = 4$), $N = 3$ to homotrifunctional monomer ($f = 6$), and so on. Thus, overall functionality of homo-*N*-functional monomers for chain polymerization is $f = 2N$. Typical homobifunctional monomers serve as crosslinking agents during chain polymerization (see Scheme 1.6) [2, 37, 38].

The feature $f > 2$ for homo-*N*-functional monomers is related to crosslinking and gel formation of step-growth polymerization as already explained earlier by
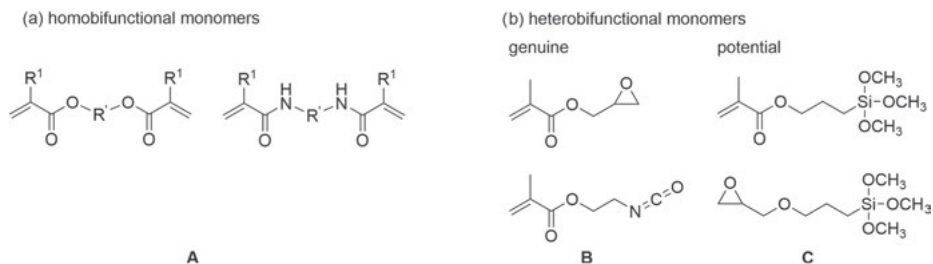
Scheme 1.6: Examples of homo- and heterobifunctional monomers. The homobifunctional monomers are bisacrylates and bisacrylamides (R^1 = H, CH_3; R^2 is usually an acyclic or cyclic alkyl group). Genuine heterobifunctional monomers are 2,3-epoxypropyl methacrylate and 2-isocyanoethyl methacrylate. The two potential heterobifunctional monomers are (3-glycidyloxypropyl)trimethoxysilane and 3-(trimethoxysilyl)propyl methacrylate.

Equation 2. In contrast, in the case of step-growth monomers, overall functionality of a homo-N-functional monomer is $f = N$.

Heterobifunctional monomers combine two polymerizable groups, which are completely different in their chemical structure, in one molecule. Scheme 1.6 shows some examples for homo- (**A**) and heterobifunctional monomers (**B** and **C**).

Heterobifunctional monomers of the type presented in Scheme 1.6 are potential candidates for the production of type C or class II hybrid materials (Fig. 1.2). In the broadest sense, class II hybrid materials can be classified as copolymers from two networks. The most important factor of heterobifunctional monomers is that the functionality of the non-polymerizing group increases during homopolymerization.

Polymerizable groups of genuine heterobifunctional monomers, such as acrylate, epoxide, or isocyanate, are immediately usable. The methoxysilyl group (or other M−O−R groups) is not directly usable because it must be transformed into Si−OH by reaction with water. Thus, for alkoxysilyl compounds, the actual functionality is also a function of conversion with water. Therefore, it must be distinguished between genuine and potential heterobifunctional monomers.

The nomenclature for heterobifunctional monomers in literature is not always according to rules of International Union of Pure and Applied Chemistry (IUPAC). Thus, 2,3-epoxypropyl methacrylate was named as "Jekyll and Hyde" monomer because it can enter into both vinyl and ROP [39]. Also, the name "tandem" monomer is sometimes used for this type of heterobifunctional monomer to demonstrate the concurrence of two differently polymerizable groups within one molecule [40, 41].

In case that a heterobifunctional monomer possesses one polymerizable group for chain polymerization and another one for step-growth polymerization, the determination of f of the single monomer depends on whether both groups can react with each other. If they do not react with each other, the functionality results from each chemically reactive group individually. For this purpose, two different

abbreviations for the respective functionalities are useful; f_{SG} for the functionality of the step-polymerizable groups and f_{CP} for the chain-polymerizable groups.

In the following, the complex scenario for polymerization of 3-(trimethoxysilyl)-propyl methacrylate (TMMA) will be discussed as an example. The functionality f of TMMA with regard to potential step-growth polymerization of trimethoxysilyl group is three ($f_{SG} = 3$) and with regard to chain polymerization (acrylate double bond), it is two ($f_{CP} = 2$). The situation changes if either chain polymerization of TMMA by methacrylate groups or step-growth of trimethoxysilyl groups starts. The crucial aspect of heterobifunctional monomers is that the functionality of the group not involved in the polymerization increases linearly with the degree of polymerization. This scenario is shown for $CH_2=CH-R-Si(OR')_3$ and $CH_2=CH-R-SiR''(OH)_2$ as hypothetical monomers in Scheme 1.7. The latter would result from $CH_2=CH-R-SiR''(OR''')_2$ after hydrolysis.

The difference in functionality f of chain and step-growth polymerization ability as a function of water conversion of a TMMA-related model monomer $(R'O)_3Si-R-CH=CH_2$ is illustrated in Table 1.1 (see also Scheme 1.7). $x/1$ represents the water/monomer ratio corresponding to the resulting species if complete conversion of the $-Si(OR')_3$ group takes place.

For instance, the overall functionality f of the potential step-growth moiety $-Si(OR')_3$ increases with increasing degree of polymerization in the following manner. Assuming an average DP_n of 10 of the formed oligomer regarding the ethylenic moiety, then the overall functionality f_{SG} with respect to the fully hydrolyzed $-Si(OH)_3$ moiety is 30 according to Equation 2. Then, only about 6.7 % of the silanol group conversion to Si−O−Si linkages is sufficient for crosslinking of the formed polymer to take place. For a DP_n of 100, the conversion of silanol groups can be below 1 % to guarantee gel formation. Therefore, only a low quantity of generated silanol groups is sufficient for gel formation to take place when the vinyl group part begins to polymerize. The
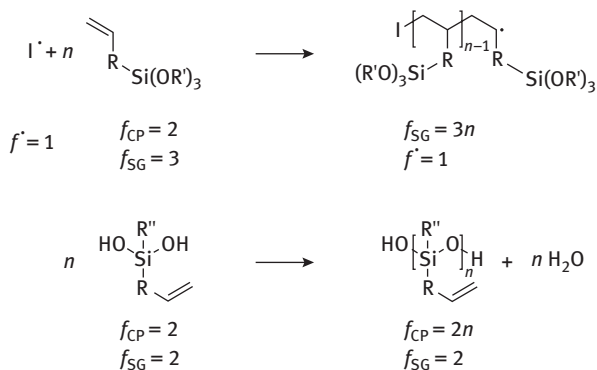
Scheme 1.7: Demonstration of the influence of the degree of polymerization n on the resulting functionality f_{SG} and f_{CP}, of the respective group not involved in radical chain polymerization of $CH_2=CH-R-Si(OR')_3$ (f_{SG}) or step-growth polymerization of $CH_2=CH-R-SiR''(OH)_2$ (f_{CP}), after complete conversion.

Tab. 1.1: Assumed molecular species by stepwise reaction of a heterobifunctional monomer of the $(R'O)_3Si-R-CH=CH_2$ type with water illustrated for the trimethoxy group hydrolysis and impact of different degree of polymerization of the vinyl group ($DP_{n,CP}$) on resulting overall functionality f_{SG} of $-Si-OH$ moieties at the formed polymer.

$x/1$	Assumed monomer species	f_{CP}	f_{SG}				
			$DP_{n,CP} = 1$	2	5	10	100
0/1	$(R'O)_3Si-R-CH=CH_2$	2	0	0	0	0	0
1/1	$HO(R'O)_2Si-R-CH=CH_2$	2	1	2	5	20	100
2/1	$(HO)_2(R'O)Si-R-CH=CH_2$	2	2	4	10	20	200
3/1	$(HO)_3Si-R-CH=CH_2$	2	3	6	15	30	300

same applies in the case of TMMA undergoing sol-gel reaction at first. Then, homo-N-functionality of the vinyl groups of the formed oligomer increases as a function of the degree of polymerization as well. Subsequently, N equals DP_n of the silicatic hybrid network. The numbers of functionalities ($f_{SG} + f_{CP}$) become completely complex if both groups are simultaneously polymerized by using initiator/catalyst mixture, etc. The fast increasing f of each polymerizing group would rapidly induce a crosslinking reaction already at the beginning of the reaction. The gel formation would hinder the further polymerization of the heterobifunctional monomer. This factor is the reason that hybrid materials syntheses which combine chain and step-growth polymerization by the sole use of heterobifunctional monomers are hard to control not only due to the different time scales at which each polymerization reaction takes place. Then, several polymerizable groups still remain intact but covalently bonded in the hybrid material. This is the typical occurrence which is observed in crosslinking polymerization and explained by the theory of gel point formation.

These considerations clearly demonstrate that the definition of individual functionalities of the heterobifunctional monomer is not helpful if the pure monomer is used in polymerization reactions.

In most cases, heterobifunctional monomers are only used in small amounts to covalently bond two polymer structures or to link polymers on surfaces. For this purpose, the use of heterobifunctional monomers has been established for the synthesis of a variety of organic/inorganic hybrid materials. Especially, TMMA and structurally related acrylic compounds are suitable as heterobifunctional monomers for producing a variety of poly(methyl methyacrylate)/silicatic hybrid materials.

Alkoxysilane compounds containing functional groups, suitable to react with polymers or surfaces, are widely available and find application in materials chemistry. (3-Mercaptopropyl)trimethoxysilane and (3-glycidoxypropyl)trimethoxysilane fall into this category.

(3-Glycidyloxypropyl)trimethoxysilane (Scheme 1.6) is a special monomer because the epoxy groups polymerize cationically and can react with silanol groups during the sol-gel reaction [41].

Mostly, trimethoxysilyl group-bearing heterobifunctional monomers such as (3-glycidyloxypropyl)trimethoxysilane and TMMA are used in combination with tetraalkoxysilanes, organic monomers or other multifunctional alkoxysilanes in step-growth copolymerization or as components in reactions with reactive polymers [42–47].

1.3 Multifunctional monomers for hybrid materials synthesis

Type A and B or class I hybrid materials (Fig. 1.2) are available by SP of two different monomers as already illustrated in Scheme 1.5. Due to the independently occurring polymerizations at SPs, phase separation of the polymers is mostly observed. In order to reduce the degree of separation, concepts have been developed to construct mono-mers in such a way that two polymers are coupled simultaneously to one another at the same time.

Two types of specially designed monomers are known which fulfill this require-ment. The first group of monomers combines functional groups for sol-gel chem-istry with those for chain polymerization in a way different from the monomers in Schemes 1.6 and 1.7. The difference is that a hydrolytically cleavable bond of the M−O−R type connects the two polymerizable moieties compared to the monomers in Scheme 1.6 [45–47]. Thus, cleavable multifunctional monomers (CMMs) contain M−O−R bonds which can readily react with water or related reagents to produce two separated monomers immediately suitable for chain and/or step-growth polymeriza-tion according to Scheme 1.8.
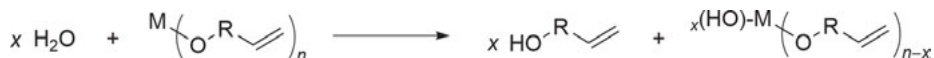
Scheme 1.8: Hydrolysis reaction of a hypothetical cleavable multifunctional monomer (CMM) which consists of n cleavable M−O−R bonds assuming conversion with x water molecules.

Representative CMMs are shown in Scheme 1.9. The chain-polymerizable group is neither covalently linked by strong C−C σ nor Si−C σ bonds (monomers of Scheme 1.6), respectively, but by a hydrolytically cleavable M−O−C bond (M = Ti, Si, B) (CMMs of Scheme 1.9). In the case of CMM, the formation of the inorganic component results from the hydrolytic instability of the M−O−C bond and its step-growth ability.

According to the definition of f, the monomers shown in Scheme 1.9 are homo-tetrafunctional with respect to chain polymerization ability ($N = 4$, $f_{CP} = 8$). Whether the monomers in Scheme 1.6 act as heterobifunctional monomers depends on the presence of a second component such as water (Scheme 1.8). This circumstance is comparable to the heterobifunctional monomer TMMA, but there is a decisive differ-ence which will be explained in the following.
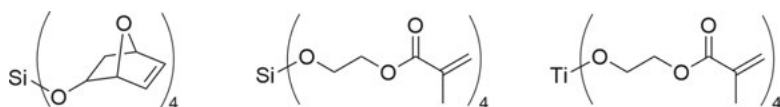
Scheme 1.9: Examples for specific heterobifunctional monomers which combine chemically reactive groups for chain and step-growth polymerization due to utilization for sol-gel process. These specific monomers are hydrolytically cleavable.

First, changes of both functionalities f for chain polymerization and step-growth ability of a common hypothetical $M-(O-R-CH=CH_2)_n$ monomer as a function of conversion with water x (Tab. 1.2) in comparison to a $(R'O)_3Si-R-CH=CH_2$ monomer (Tab. 1.1) have to be considered. Second, it is important to note that the *in situ* formed $HO-R-CH=CH_2$ monomer ($f = 2$) can also participate and copolymerize. In contrast to the potential heterobifunctional monomers of the type $(R'O)_3Si-R-CH=CH_2$, the functionality f for chain polymerization of $M(O-R-CH=CH_2)_n$ is dependent on the water/monomer ratio.

Tab. 1.2: Resulting molecular species by stepwise hydrolysis of composite monomers of the $M-(O-R-CH=CH_2)_n$ type illustrated for $n = 4$ and the resulting functionality of the appropriate polymerizing group. $x/2$ represents the water/monomer ratio corresponding to the resulting species if complete conversion takes place.

$x/2$	Assumed species	f_{CP}	f_{SG}
0/2	$M(O-R-CH=CH_2)_4$	8 (Crosslinking)	0 (No polymerization)
1/2	$HO-M-(O-R-CH=CH_2)_3$	6 (Crosslinking)	1 (Only dimerization)
2/2	$(HO)_2-M-(O-R-CH=CH_2)_2$	4 (Crosslinking)	2 (Linear chain formation)
3/2	$(HO)_3-M-(O-R-CH=CH_2)$	2 (No crosslinking)	3 (Crosslinking)
4/2	$(HO)_4M$	0	4 (Crosslinking)

This consideration is of importance to illustrate the different requirements for fabrication of nanostructured organic/inorganic hybrid materials when different types of heterobifunctional monomers are used.

The functionalities of the assumed species of Table 1.2 change abruptly when the resulting species $(HO)_x-M-(O-R-CH=CH_2)_{n-x}$ begin to polymerize. Then, the discussed scenarios of Scheme 1.7 and Table 1.1 additionally play a role. It is an important factor that mixtures of all assumed species in Table 1.2 can be simultaneously involved in the actual polymerization process. Therefore, whether a class I or class II hybrid material is formed from a CMM does also depend on the portion of water added and in which sequence chain and step-growth polymerization are externally triggered.

An advantage of this type of CMM type is the potential high functionality of each kind of the two polymerizing groups. Therefore, both formed polymers crosslink immediately which prevents the phase separation. But in contrast to the

non-cleavable heterobifunctional monomers, the functionalities of f_{CP} and f_{SG} are coupled to each other in another way. With increasing conversion of M–O–R, they are opposite (Tab. 1.2).

With regard to monomers in Schemes 1.8 and 1.9, the chain and step-growth polymerization takes place individually for each polymerizing group. Both mechanisms, chain and step-growth, are not coupled with each other on the molecular level. Thus, an initiator (for the chain-addition polymerization) as well as a catalyst and water as reactant (for the step-growth reaction) are required for the synthesis. Thus, the consecutive or SP of this type of specifically designed monomers can produce a mixture of Class I and Class II hybrid materials, depending on the stage of polymerization. It is also possible that hydrolysis takes place as post-reaction altering the Class II hybrid material to Class I.

These considerations show the restrictions of the concept of those heterobifunctional monomers. However, the manifold combination of heterobifunctional monomers with different types of common co-monomers, either suitable for chain or step-growth polymerization, opens a wide field for synthesizing hybrid materials with desired composition. As mentioned, this subject has been discussed in many review articles and textbooks [8–12, 48, 49].

To produce fine-tuned nanostructured hybrid materials, both the inorganic and organic polymer component within the hybrid material must be generated at the same time. As shown, established heterobifunctional monomers (Scheme 1.6) and hydrolytically cleavable monomers (Scheme 1.9) combine two polymerizable moieties, one for step-growth and one for chain polymerization. Thus, the functionality of each polymerizable fragment during polymerization of CMM is dependent on conversion of the covalently attached polymerizable group at the formed polymer backbone. That is explained by data from Tables 1.1 and 1.2.

Common monomers for genuine step-growth polymerization have a fixed functionality. Therefore, complex monomers are required which contain two step-growth moieties combined in such a way that both polymerizations take place mechanistically coupled and both polymers are formed simultaneously at the same time scale. Conceptually, this feature can be realized by so-called twin monomers [50–58]. Twin monomers belong to the class of heterobifunctional monomers which contain two polymerizable groups suitable for step-growth polymerization. There are two step-growth polymerizable molecule fragments covalently linked in the twin monomer. The functionalities of the two polymerizable units are fixed because no second component, such as water, is required.

As representative example, the formation of phenolic resin/silica hybrid material from 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] twin monomer (Si-Spiro) is briefly mentioned in this introduction (Scheme 1.10).

According to the principles of polymerization processes, twin polymerization of 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] can also be considered as rearrangement condensation reaction finally providing phenolic resin and silica within one hybrid
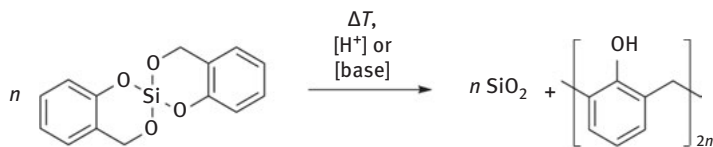
Scheme 1.10: The twin polymerization of 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline]. For this twin poly-
merization, the functionalities of the silicon moiety with $f = 4$ and for the phenolic resin with $f = 3$
are fixed. Aspects of functionality of twin monomers are treated in Chapter 2.1. Please notice,
various linkages (*o,o′-, o,m-, o,p-*) are possible.

material. A twin monomer is a specifically constructed multifunctional monomer that
polymerizes in a step-growth reaction in one process to give two polymers. The forma-
tion of both polymers takes place mechanistically coupled with each other. Therefore,
twin polymerization is examined as novel polymerization principle.

For this purpose, the availability of polymerizable twin monomers is a prerequi-
site. Twin monomers can be widely designed by using a variety of organic fragments
suitable for step-growth polymerization and inorganic elements such as the metals
and semimetals Ti, Sn, B, Si, etc. Furthermore, functional groups suitable for chain
and step-growth polymerization can be chemically introduced and substitutions of
heteroatoms (O) by other elements such as sulfur or nitrogen are possible. Thus, twin
polymerization is a modular concept. The versatile concept, the theory, and the appli-
cation of twin polymerization as a novel polymerization principle for the fabrication
of various hybrid materials are addressed in this textbook. The general concept for
twin polymerization is discussed in Chapter 2.

1.4 Conclusion

The introduction describes principle polymerization processes and aspects of mono-
mers suitable for this purpose. Special attention is given to organic/inorganic hybrid
materials synthesis and the monomers for their fabrication. To recapitulate, the defi-
nitions of the types of monomers suitable for the synthesis of linear polymers and
hybrid materials production are summarized below.

(a) A–A, A–B, and B–B monomers are suitable for (linear or cyclic) step-growth
    polymerization. Each monomer possesses the functionality of two. Importantly,
    the molecular structure of the A- or B-chemical functional group decides whether
    A (or B) does only react with B or also with itself at chosen reaction conditions.

(b) An olefin with one double bond or an appropriate cyclic compound such as an
    epoxide is a monomer with the functionality of two for linear chain polymerization.

(c) A homobifunctional monomer contains two groups, according to (b), suitable
    for chain polymerization. Then, the overall functionality is four. Thus, a related
    homotrifunctional monomer possesses a functionality of six, and so on. Avoid

the confusion of homobifunctional monomer with A–A or B–B-type monomers because homo-N-functional monomers for step-growth polymerization are A_n or B_n monomers with $n = 3, 4, 5, ...$ An odd number of functionality is not possible for homo-N-functional monomers which are suitable for chain polymerization and ROP.

(d) Principally, a heterobifunctional monomer contains one or more groups suitable for chain polymerization and/or step-growth polymerization which are linked covalently together *via* a spacer or by ionic character. The number of functionality of each moiety is determined by the same criteria mentioned under (a), (b), and (c). However, functionalities are not only dependent on the initial monomer but are also dynamically changed as soon as the polymerization starts. Each individual polymerization, step-growth and chain polymerization, of the heterobifunctional monomer takes place mechanistically independent of each other.

(e) There are two types of heterobifunctional monomers to distinguish depending especially on whether the chemical bond is cleavable or not by water or other reagents during polymerization.

(f) Hydrolytically cleavable heterobifunctional monomers and twin monomers are specifically designed monomers which can form two polymers in the course of the cross-polymerization process.

(g) A twin monomer is a specially designed monomer which contains different inorganic and organic fragments suitable for two or more different step-growth polymerization processes. Both polymerization processes take place mechanistically coupled with each other by use of solely one catalyst or other stimuli like heat or light.

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