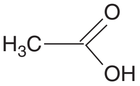
1

Introduction

1.1 Special Features of Polymers

Why write a book especially on modeling of polymerization reactions? To answer this question, it is best to compare the production of polymers with the production of low-molecular-mass compounds and to see what is special for polymers. For example, to produce acetic acid



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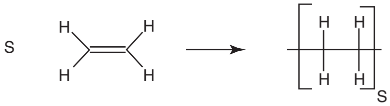
several processes can be followed. Rather old ones, already known to the ancient Egyptians and Greeks, used the biotechnology way from grapes via ethanol to vinegar. Or more modern techniques like the oxidation of acetaldehyde by oxygen and $Mn(OAc)_2$ as catalyst, the air oxidation of butane at high pressures or the Monsanto process, the addition of carbon monoxide to methanol catalyzed by rhodium complexes. Despite the variety of raw materials and processes, all end with acetic acid with the structure shown earlier. The various processes only differ in terms of raw material, conversion, yield, selectivity, concentration, and kind of impurities; and the engineering task is to optimize these quantities, the product being in all cases acetic acid with defined properties.

This is by far not the case with polymers. Let us have a look at a simple polymer like polyethylene. It can be produced by several different mechanisms – by radical polymerization to give low-density polyethylene (LDPE) with short- and long-chain branches, or catalyzed by various transition metal catalysts from chromium, titanium, and so on to high-density polyethylene (HDPE) or linear low-density polyethylene (LLDPE) by opening the double bond of ethylene and linking s monomers to chains of length s.



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However, even for such a simple polymer like polyethylene, there exists a wide variety of grades that differ in properties like viscosity, crystallinity, transparency,

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gloss, and so on, which means that these grades have different molecular structures; so polyethylene is not just polyethylene. One obvious difference between two polyethylene molecules might be the number s of monomeric units in the chain, the degree of polymerization. In contrast to biological macromolecules like enzymes, DNA, and RNA, which have well-defined structures despite being polymers, synthetic macromolecules (and also many of the biopolymers like cellulose, lignine, etc.) differ at least in length s, and consist of an ensemble of chains with different chain lengths – they have a chain-length distribution. There might be more structures differentiating polymer chains from each other, and we come back to the kind of structural differences later in Section 1.2. These molecular structures determine the properties which the polymer will show during processing and in their final application. The molecular structure, however, depends strongly on the chemistry, the kinetics, and the process conditions.

Therefore, the challenge for chemists and engineers in the development and production of synthetic polymers is not only to optimize yield, conversion, and so on but also to produce the right molecular structure to meet the desired application and processing properties.

Here, suitable mathematical models linking reaction kinetics and process conditions to the resulting structure will be of great help to overcome this challenge. Especially if we consider that for polymers, in contrast to low-molecular-mass compounds where we have distillation, extraction, crystallization, and other purification methods, there does not exist any separation method – except on an analytical scale – to separate polymers with the desired structure from “bad” polymers. So, the polymerization process itself must yield the desired structure at once.

There is another important difference between processes for polymers and low molecular compounds. We have to consider that the chain length s might be several hundreds or thousands or even higher. This means that the molecular mass (which is given by s times molecular mass of the monomer unit) can be as high as several 10^5 or even 10^7 g/mol, so we have to consider processes where a low molecular compound, the monomer, with a low viscosity like water reacts to products with much higher viscosity, which may be up to 10^5 Pa s. In the latter processes, however, we convert low-molecular-mass compounds to other low-molecular-mass chemicals, and viscosity will not change very much and will be $10^{-3} - 10^{-2}\ \text{Pa} \cdot \text{s}$ or even lower if we deal with processes in the liquid or gaseous state.

This dramatic change in viscosity has several implications. So, mixing becomes an issue. Poor mixing causes inhomogeneity with respect to concentration, and also to temperature. We have to keep in mind that polymerization reactions are usually rather exothermic reactions (see Table 1.1) with adiabatic temperature rising up to several hundred or thousand K. High viscosity will impede heat removal capacity tremendously and may cause hot spots in the reactor that may lead to side reactions or even runaways.

In addition, this high viscosity may affect the reaction kinetics itself, as in some cases reaction rates become mass-transport limited. The high viscosity might impede the diffusion of long chains or even of monomers. We come to this point when considering radical polymerization.

Table 1.1 Heat of polymerization of some example monomers [3, 4].

Monomer	General formula	$-\Delta H_{r,.}$ (kJ/mol)	$-\Delta T_{ad}$ (K)
Ethylene, propylene, styrene, vinyl esters, acrylic acid and -esters, dienes	$H_2C{=}CHX$	67–105	300–2000
Isobutene, α-methyl styrene, methacrylic acid and esters	$H_2C{=}CXY$	33–59	140–400
ϵ-Caprolactame, 2-pyrrolidone (γ-butyrolactame)		0–17	0–70

Another aspect that is of practical importance, but is often underestimated, is the high demand for purity of the involved chemicals. The concentration of active species is often rather low; in radical polymerization, the concentration of growing chains is $10^{-8} - 10^{-7}$ mol/l, the concentration of active species in transition-metal-catalyzed polymerization is just one or two orders of magnitude higher. Moreover, in some cases (living polymerization and step-growth polymerization, see Section 2.4.1), the resulting molecular mass is strongly dependent on stoichiometry; here, small errors may prevent us from reaching the desired values.

1.2 Structures in Polymers and Their Influence on Processing and Application Properties

Polymers are used not because they have a certain structure, but because they have certain properties in their final application or during processing. However, the results of kinetic or process models are usually not these final properties but information about the molecular structure of the macromolecules. In the following, we briefly discuss possible structural differences of polymers and some consequences of their properties. This is by far not an exhaustive overview and is greatly simplified. It shall more serve as an appetizer and motivator to use modeling methods to design polymer structures.

1.2.1 Chain Length, Molecular Mass, Moments, and Mean Values

In Section 1.1 we have already pointed out that one important structural property of a macromolecule is its degree of polymerization resp., its molar mass. Synthetic macromolecules usually have a *distribution* of degrees of polymerization resp. molar masses.

Definition 1 *By $P_s(t)$ we denote the concentration of chains of degree (chain length) s of polymer P at time t. Therefore, this quantity is related to the number of molecules of a certain kind. (Figure 1.1a,c). The distribution $P_s(t)$ is called frequency or number distribution.*

It can also be represented in terms of the molecular mass of the respective chains (Figure 1.1b,d) and as differential (Figure 1.1a,b) or integral distribution

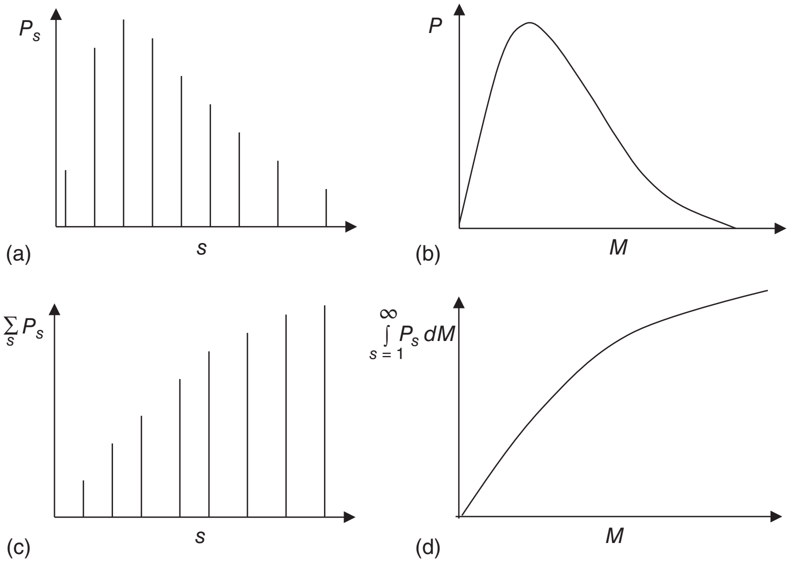


Figure 1.1 Possible representations of distributions: (a) discrete, differential frequency, or number distribution of degree of polymerization, (b) continuous differential frequency or number distribution of molar mass, (c) discrete, cumulative distribution of degree of polymerization, (d) continuous, cumulative distribution of molar mass.

(Figure 1.1c,d). Very often, however, one is interested in the *mass* of polymer molecules. The mass of a chain consisting of s single molecules is given by the weighted sum of these units. Let $M^P_{\overline{M}}$ denote the *average molecular mass per monomer unit* (AMW) in all chains of type P. In the simplest case of homopolymers, $M^P_{\overline{M}}$ is just the molar mass of the monomer. We remark, however, that in complex systems, for example, copolymerization, $M^P_{\overline{M}}$ may be a time-dependent function of polymer composition (see (2.287)). Then, the mass of a chain P_s is $s \cdot M^P_{\overline{M}}$. Therefore, the *weight* or *mass* distribution of mass of a polymer P is given by

$$W^P_s(t) = P_s(t) \cdot s \cdot M^P_{\overline{M}} \tag{1.3}$$

We have to keep in mind that all these distributions are functions of a discrete variable, as the degree of polymerization can only have integer values $1, 2, \ldots, s$. For long chains ($s \ll 1$), we could deal with them as continuous functions; however, this requires additional assumptions and in view of the fact that this problematic approach is not allowed for short oligomers, we will not discuss it here.

A third important representation of a distribution is induced by the measurement of the molar mass distribution by gel permeation chromatography (GPC). It has been shown [5] that the GPC data are *proportional* to a distribution

$$W^P_{\log M}(t) = P_s(t) \cdot s^2 \cdot \left(M^P_{\overline{M}}\right)^2 \tag{1.4}$$

The meaning of this distribution is less intuitive than the mass distribution, but it is apparent that the concentration of long chains is amplified by the factor s^2. In many modeling projects, it is crucial to analyze all three types of distributions.

We also note that the numerical approximation of $W^P_{\log M}$ can be much more challenging than to obtain the basic frequency distribution.

In many cases, distributions are just characterized by some average values. For that we introduce the *statistical moments* of type k and of distribution P at time t

$$\lambda_k^P(t) = \sum_{s=1}^{\infty} s^k P_s(t) \tag{1.5}$$

Remark 1 (moment notation) *There are very different notations in use for moments, often the Greek letter μ instead of λ is used. The summation bounds are often omitted as well as the superscript, if there is only one distribution being considered.*

Remark 2 (moment meaning) *The meaning of the zeroth moment λ_0^P is the total concentration of polymer chains P_s. The meaning of the first moment λ_1^P is the total concentration of all monomer units in all chains of polymer P_s.*

Using the first moment λ_1^P of a given polymer distribution P_s and the average molecular mass per monomer unit $M^P_{\overline{M}}$, the mass concentration m^P of a polymer species can be described by

$$m^P = \lambda_1^P M^P_{\overline{M}} \tag{1.6}$$

In some models, particularly in polycondensation, each single polymer chain may carry or (miss) one additional piece of mass, a fragment, of molecular weight $M^P_{\overline{F}}$. Then the expression (1.6) has to be extended by a term that multiplies the total number of polymer chains λ_0^P with the mass of the fragment. Note that $M^P_{\overline{F}} < 0$ is possible and allowed here.

$$m^P = \lambda_1^P M^P_{\overline{M}} + \lambda_0^P M^P_{\overline{F}} \tag{1.7}$$

Next, we use the statistical moments to define some important mean values. The *number average* describes the average number of monomer units per chain. The *mass average* leads to the average number of monomer units in a macromolecule to which a randomly chosen monomer unit belongs.

$$N_n^P(t) = \frac{\lambda_1^P(t)}{\lambda_0^P(t)}, \quad \text{number average chain length} \tag{1.8}$$

$$N_w^P(t) = \frac{\lambda_2^P(t)}{\lambda_1^P(t)}, \quad \text{weight average chain length} \tag{1.9}$$

Remark 3 *We use the capital letter N to characterize the average values instead of the often used notation $\overline{P_n}$ or $\overline{P_w}$, as we have reserved the letter P to describe the polymer.*

Remark 4 *We have to add the superscript P in these definitions, since in nearly all situations of interest we have to distinguish different types of polymers. However, outside a model consideration and without a concrete polymer, we will use just N_n, N_w, PDI.*

Often, people are more interested in the corresponding mass averages, only extended by a factor given by the average molecular mass of a monomer unit:

$$M_n^P(t) = \frac{\lambda_1^P(t)}{\lambda_0^P(t)} M_{\overline{M}}^P \left[\frac{mass}{mol}\right], \quad \text{number average molecular mass} \tag{1.10}$$

$$M_w^P(t) = \frac{\lambda_2^P(t)}{\lambda_1^P(t)} M_{\overline{M}}^P \left[\frac{mass}{mol}\right], \quad \text{weight average molecular mass} \tag{1.11}$$

The important width of the distribution is characterized by the *polydispersity* index (PDI)

$$\text{PDI}^P(t) = \frac{\lambda_2^P(t)\lambda_0^P(t)}{\left(\lambda_1^P(t)\right)^2} = \frac{N_w^P(t)}{N_n^P(t)} = \frac{M_w^P(t)}{M_n^P(t)} \tag{1.12}$$

Note that PDI can be correlated to the standard deviation σ usually used in statistics to characterize the width of a distribution by

$$\text{PDI} = \left(\frac{\sigma}{N_n^P}\right)^2 + 1 \tag{1.13}$$

1.2.2 Rheological Properties

Many of the mechanical and rheological properties of polymers come from the fact that in contrast to small molecules, macromolecules do not exist as separated molecules (except in highly diluted solutions), but are more or less "entangled" (see Figure 1.2). These entanglements act as physical cross-links which drastically hinder the mobility of polymer chains and consequently influence all properties that are connected to chain mobility. Solid-state properties like tensile strength and impact strength usually increase with N_w^P. In contrast to this, the rate with which a crack propagates in a polymeric material is reduced for higher molecular masses. So, in terms of mechanical properties, high molar masses are desirable. However, the entanglement is also responsible for the extreme high viscosity of polymer melts and concentrated polymer solutions. Viscosity η is the

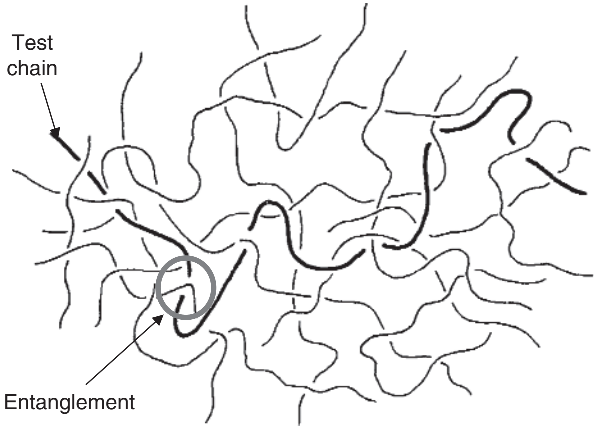


Figure 1.2 Schematic entanglement of bulk polymers.

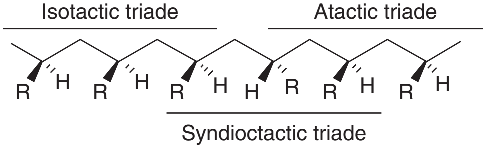
ratio of shear stress τ and shear rate $\dot{\gamma}$, for example, the resistance of a liquid to replacement. In "normal" liquids, according to Newton's law $\tau = \eta\dot{\gamma}$, viscosity is a constant. For polymer melts and highly concentrated solutions or other more complex liquid systems like dispersions, suspensions, and so on, this simple relation is no longer valid, but η becomes a function of $\dot{\gamma}$. The mostly observed phenomenon with polymer systems is the so-called shear-thinning behavior, where viscosity decreases with shear rate, because by shearing more and more entanglements are released. This is sketched in Figure 1.3.

Here, the viscosity at low shear rates, the zero-shear viscosity, correlates with N_w^P very strongly; above a critical chain length N_c^P from which on entanglement occurs, the correlation $\eta_0 \sim (N_w^P)^{3.4}$ holds for nearly all linear polymers. However, not only the average values influence the shear viscosity but also the distribution itself (Figure 1.4). Broader distributions usually show a stronger shear-thinning behavior, which makes processing easier while maintaining a high molecular mass for mechanical properties.

There are far more properties which depend on chain length, like glass transition temperatures T_g, melting point T_m of semi-crystalline polymers, viscoelastic behavior, and others.

1.2.3 Constitutional Isomers

As in low molecular compounds, in macromolecules also all kinds of constitutional isomers may occur.



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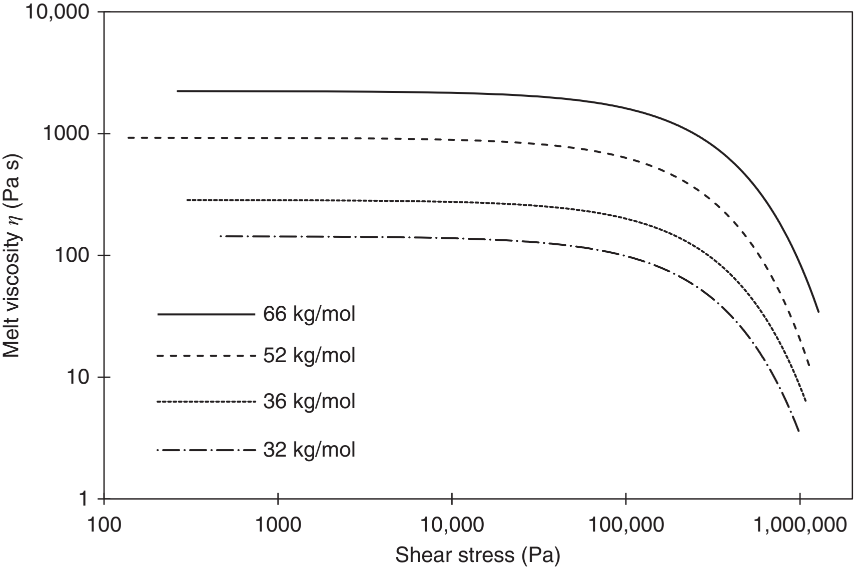


Figure 1.3 Shear viscosity curves for polyethylene with different weight average molar mass.

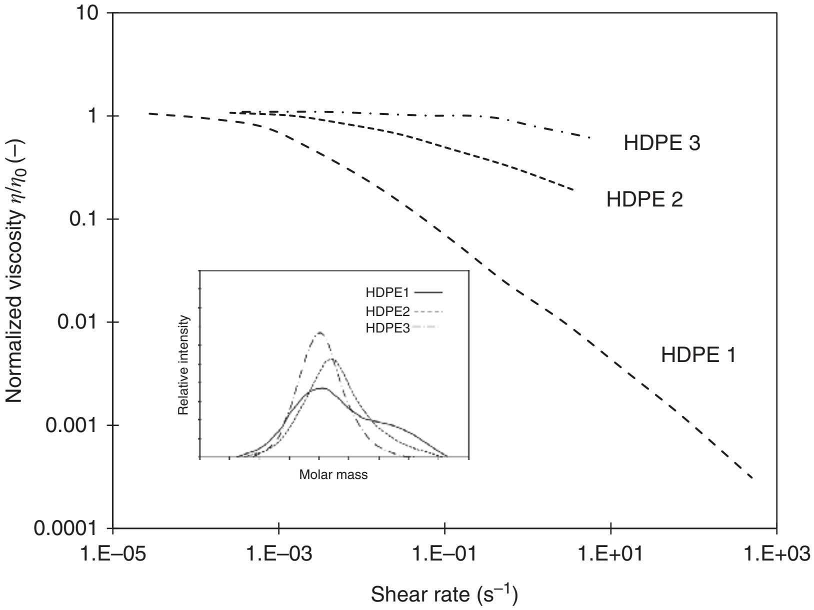
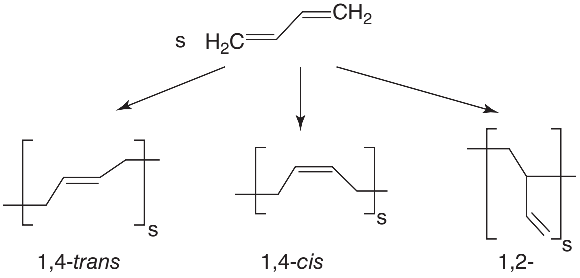


Figure 1.4 Shear viscosity curves of polyethylene grades with different molar mass distributions (normalized to same zero-shear viscosity).

If the monomer unit has an asymmetric carbon atom, the macromolecule may show stereoisomerism. It may consist of isotactic sequences, where the substituent R is always on one side of the plane, syndiotactic sequences where the position of R alternates, or atactic sequences with no regularities. Stereospecific polymers often result from transition-metal-catalyzed polymerization like isotactic polypropylene with Ziegler catalysts. The degree of stereoregularity has a strong effect on melting point, degree of crystallization, or glass transition temperature, and so influences mechanical and optical properties. It is usually characterized by the concentration of the respective triades or pentades.



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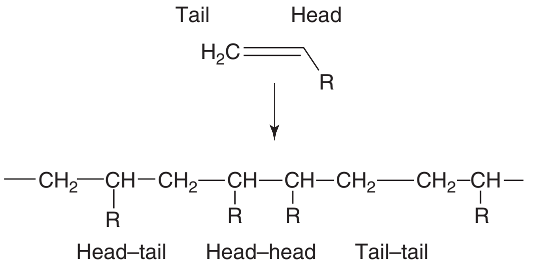
Geometric isomers may occur, for example, during the polymerization of dienes, when there are several possibilities to open a double bond as in the polymerization of butadiene depending on the process and catalysts/initiators. This results in 1,4-*cis*, 1,4-*trans*, or 1,2-polybutadienes with remarkably different properties. Polybutadienes produced with Co- or Ni-catalysts show >95% 1,4-*cis* content with $T_g \approx -105\,^\circ\mathrm{C}$ and are partly crystalline with $T_m \approx 2-3\,^\circ\mathrm{C}$, high 1,2-polybutadiene produced with Li-organyls shows 1,2-content of $\approx 90\%$ and has $T_g \approx -5\,^\circ\mathrm{C}$ and $T_m \approx 155\,^\circ\mathrm{C}$. In emulsion polymerization, one may obtain mixed structures with $\approx 10\%$ 1,4-*cis*, $\approx 70\%$ 1,4-*trans*, and $\approx 20\%$ 1,2-structures and $T_g \approx -80\,^\circ\mathrm{C}$. Consequently, they differ in their application properties as tire rubbers in abrasion resistance, rolling resistance, road holding, and so on.



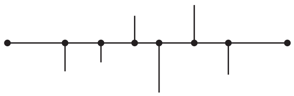
(1.16)

Other structural isomers may occur with nonsymmetric monomers from the orientation during the addition of the monomer to the active center. There is an agreement that the carbon atom with the larger substituent is called the head of the monomeric unit, and for asymmetric monomers there exist three possibilities of orientation. Head–tail is the "normal" orientation, and irregularities like the head–head or tail–tail addition usually influence properties like the degree of crystallinity.

1.2.4 Architectural Isomers

Until now we have considered macromolecules to be linear molecules; but in many cases, this is not true. There might exist a wide variety of different architectures with the same molar mass.

Comblike or graft polymers:



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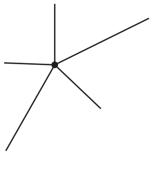
Starlike polymers:



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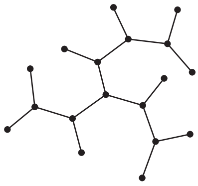
Treelike polymers:



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(long-chain) Branched polymers

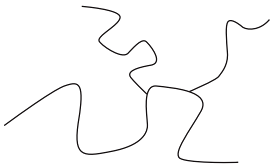

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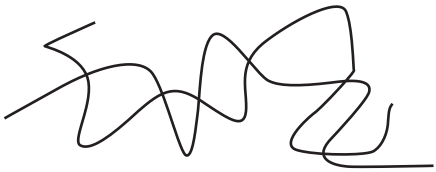
Figure 1.5 shows how the architecture may influence properties. The viscosity of starlike polymers is lower than that of the linear polymer with the same molar mass, because the coil radius of a starlike polymer is smaller than that of linear molecules of the same molecular mass.

A special class of polymer architectures are cross-linked polymers. Polymer chains in a network have at least two cross-linking points by which they are connected to other chains of the network; so, a polymer network, in principle, consists of just one molecule. Polymer networks may be built during the polymerization process itself or may be formed starting from linear chains which then will be cross-linked in a separate process (vulcanization). It is a special challenge to describe their structural properties, like the concentration of cross-links, the chain length between cross-links, and so on. Depending on the degree of cross-linking, polymer networks may be soft, elastic, and swellable (like superabsorbent polymers, rubber tires), or they may be hard and brittle (as in the case of phenol-formaldehyde resins, Bakelite®, the earliest commercial synthetic resin)



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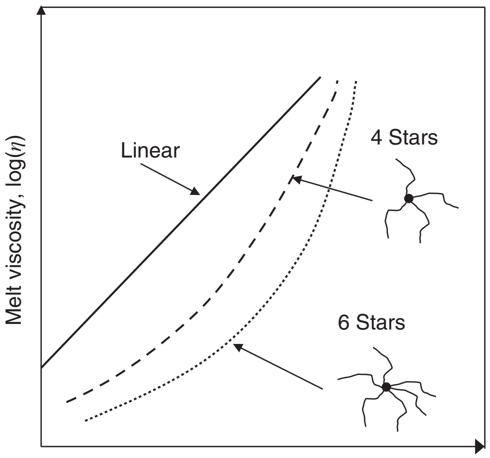

Figure 1.5 Schematic dependence of melt viscosity on molar mass for different architectures.

1.2.5 Copolymers

Only a few commercial polymers consist of just one monomer; most of them are copolymers of two or more monomers, $M_1, M_2, \ldots, M_i$. The obvious difference between copolymers is their composition, that is, the fractions $F_1, F_2, \ldots, F_i$ of the monomer i in the polymer. However, copolymers of the same overall composition may differ in the sequence of the different monomers along the chain. Most common are so-called "statistical" copolymers where the monomer units are randomly distributed along the chains. We see in Section 2.6 that they obey certain statistics; for example, they can be treated as Markov chains of zeroth, first, or second order. Strongly alternating copolymers can be obtained if neither of the two monomers is able to form a homopolymer. Finally, block copolymers may be formed by sequential addition of different monomers to living initiators (see Chapter 2) or by coupling of separately formed homopolymers.

Statistical copolymers: $-M_1M_1M_2M_1M_2M_2M_1M_2M_1M_1-$
Alternating copolymers: $-M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1-$
Block copolymers: $-M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2-$

It is obvious that these different structures may cause tremendous differences in the physical and application properties of copolymers. This is exemplified in Figure 1.6 for the glass transition temperature of a block and a statistical copolymer. Block copolymers show two glass transition temperatures, being those of the two homopolymers. Statistical copolymers only show one glass transition temperature that is somehow the average of the glass transition temperatures of the homopolymers.

There are several characteristics by which the monomer sequence along the chain can be described. As with the degree of polymerization, we also have to deal with distributions, so there are characteristics describing average values like the average sequence length of monomer M_1 describing how many units M_1 (on average) follow one after the other without being interrupted by another monomer.

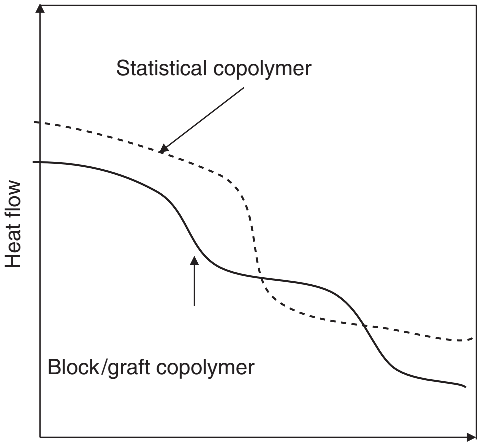

Figure 1.6 Typical glass transition temperature behavior of statistical and block copolymers.

There are several methods to take into account the distribution properties. One possibility is to use the sequence length distribution, which gives the fraction of sequences with $1, 2, 3, \ldots, s$ units M_i. Another possibility to look at the distribution is to characterize a copolymer according to the fraction of triads or pentads around the central unit M_i (see Figure 1.7), that is, what are the direct neighbors of M_i or even the next but one neighbor.

We come to these characteristics in more detail in Section 2.6. Furthermore, naturally also for copolymers, there may exist architectural isomers, as described in Section 1.2.4. Here, the main and side chains may all consist of statistical copolymers, or the main and side chains may consist of different polymers, or any other possibility as shown here

$$
\begin{array}{cccccccccccccccccc}
M_1 & M_2 & M_1 & M_2 & M_1 & M_1 & M_2 & M_1 & M_1 & M_2 & M_2 & M_1 & M_1 & M_2 & M_1 & M_2 & M_1 & M_1 \\
 & M_2 & & M_2 & & & & & & M_2 & & & & & & M_2 & & \\
 & M_2 & & M_2 & & & & & & M_2 & & & & & & M_2 & & \\
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 & & & & & & & & & M_2 & & & & & & & & \\
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M_1 & M_2 & M_1 & M_2 & M_1 & M_1 & M_2 & M_1 & M_1 & M_2 & M_2 & M_1 & M_1 & M_2 & M_1 & M_2 & M_1 & M_1 \\
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M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 & M_1 \\
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\end{array}
\tag{1.22}
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Therefore, the introduction of more than one monomer increases the number of possibilities for the structure of macromolecules dramatically. A simple

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M_1 - M_1 - M_1 \\
M_2 - M_1 - M_2 \\
M_2 - M_1 - M_1
\end{array}
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$$

Figure 1.7 M_1-centered triads and pentads.

example will demonstrate this. Imagine a copolymer consisting of equal moles of two monomers, for example, styrene (S) and methyl methacrylate (MMA), and the distribution of degrees of polymerization of this polymer has a number average of $s = 1000$. Now let us ask how many macromolecules with this average chain length 1000 and the average composition of 500 styrene and 500 MMA units may exist. This is equivalent to the question of how many possibilities do exist to put k coins into n places (irrespective of the sequence). From combinatorial analysis, we know that this number is

$$\binom{n}{k} = \frac{n!}{(n-k)!k!}$$
$$\binom{1000}{500} = \frac{1000 \cdot 999 \cdot \cdots \cdot 501}{500!} = 2.70 \times 10^{299} \tag{1.23}$$

For our example and in view of symmetry, this yields 1.35×10^{299} possibilities. The molar mass of such a chain ($M_S = 104$, $M_{MMA} = 100$ g/mol) then is 102,000 g/mol, and we get the absolute mass of one chain as 1.7×10^{-19}g by dividing the molar mass by N_A. Thus, if we had the task of synthesizing one molecule for all of the possibilities, we end up with the production of 2.3×10^{274} t. The mass of our galaxy is assumed to be in the range of 10^{40} t. So, it is rather unlikely that we ever have produced two identical molecules of this kind. Moreover, here we just have considered one kind of isomerism, that is, the positioning of the monomer. The other types of isomerism mentioned will amplify the possibilities of how a macromolecule with a definite chain length (=molar mass) and a certain composition may look like in all detail.

This shows that especially for synthetic polymers, it is difficult to look at individual molecules. We should better characterize them by some averaged quantities; some of them have been introduced in this chapter, and they – and additional ones – are described in detail when appropriate. Nevertheless, there might be cases where we will have a look at individual species (see Section 5.5).

1.3 Some Analytical Methods for Model Validation

The main purpose of the models we are dealing with is to link information about the structure of the macromolecules and the process for producing these molecules. The mathematical tools are important, but at least as important for a successful modeling project is to have analytical tools at hand which give us the structural information about the polymer. This experimental information is important for two reasons. In the beginning of a project, it will help us find a proper estimate of the model parameters – rate coefficients, distribution coefficients, and so on. In the validation phase, experimental data are used to proof the quality of the model. Table 1.2 gives some hints for possible analytical methods, but it is not exhaustive; and, in many cases, the suitable method depends on the system under investigation.

Table 1.2 Methods for determining macromolecular structures.

Model output	Measurement method	Class	Remarks
$\overline{M}_n$	Vapor pressure osmometry	A	<20 kg/mol
$\overline{M}_n$	Membrane osmometry	A	100–1000 kg/mol
$\overline{M}_n$	Cryoscopy, ebullioscopy	A	<10 kg/mol
$\overline{M}_n$	End group analysis (spectroscopy, titration)	E	<30 kg/mol
$\overline{M}_w$	Static light scattering	A	>10 kg/mol, gives radius of gyration
$\overline{M}_w$	Dynamic light scattering	A	>10 kg/mol, gives hydrodynamic radius
$\overline{M}_w$	Small-angle X-ray scattering, SAXS	A	>10 kg/mol
$\overline{M}_w$	Small-angle neutron scattering, SANS	A	>10 kg/mol
$\overline{M}_\eta$	Solution viscosimetry	R	>10 kg/mol
Molar mass distribution	Gel permeation chromatography, size exclusion chromatography	A (R)	Depending on detector
Molar mass distribution	Analytical ultracentrifuge, sedimentation velocity, sedimentation equilibrium	A	Diffusion and sedimentation coefficient
Molar mass distribution	Field flow fractionation	A (R)	Depending on detector
Molar mass distribution	MALDI-TOF	A	
Molar mass distribution	Dynamic mechanical analysis (DMA)	R	
Chemical composition	Spectroscopic methods, elementary analysis	A	Depending on system
Sequence lengths, triades, pentades in copolymers	Spectroscopic methods	A	Depending on system
Bivariate distribution in copolymers	2D chromatography (HPLC+SEC)	A, R	
Tacticity	^{1}H, ^{13}C-NMR, FT-IR	A	
Degree of short chain branching	NMR, FT-IR	A	
Degree of long-chain branching	Solid-state-NMR, FT-rheology, SEC with triple detector (RI, LS, viscosimetry)	A	
Cross-linking density	Swelling	R	Model gives chemical, analytics often chemical + physical cross-linking
Cross-linking density	Elasticity modulus, shear modulus, DMA	R	Model gives chemical, analytics often chemical + physical cross-linking

When looking at the various methods, we can classify the measurement methods into three classes (see Table 1.2):

1) Absolute methods (A) give the property without any assumptions about the chemical or physical structure of the molecule. Typical absolute methods are, for example, those measuring colligative properties (vapor pressure osmometry, membrane osmometry).
2) Equivalent (E) methods need some assumptions about the chemical structure of the molecule like for example end group titration.
3) Relative methods (R), in all cases, need calibration as they depend on the chemical structure of the solute and its interaction with the solvent, like viscosimetry.

1.4 Description of Polymer Properties

Table 1.2 shows many properties of polymers in addition to the chain length *s* we already have used in our basic Definition 1 - that is, composition, sequence lengths, tacticity, branching frequency and lengths, and so on. In principle, we can (try to) describe a polymer chain in terms of many or even all of those properties, but very often we will end up at only one or two characteristics of interest. Nevertheless, we think that readers should know a few more abstract basics of the modeling approaches described in this book.

In this section we very briefly do the following:

- Sketch the basic description of the stochastic process behind a polymerization,
- Introduce the concept of the chemical master equation (CME) that principally governs all chemical reactions, even if this fact is not always recognized,
- Show that the CME can be reduced to a simpler reaction kinetics equation (RKE),
- Show how to reduce the number of described polymer properties,
- Describe the difference between deterministic and stochastic simulation.

Let us assume for a moment that we would be able to analyze the polymer chains of a real reactor in all detail and at any time. We could pick an arbitrary number of chains (e.g., 1 mole = $6.023 \cdot 10^{23}$ molecules) and view them with all their structures, for example, the branches as in Figure 1.8 or the inner composition as in Figure 1.9.

How could we describe the information of these two pictures? For the topology, we could characterize the chain having a total chain length *s* and a number of branches with an individual (or average) length. We could also count different monomer types or analyze the exact position of the branching points. For the composition, we could consider the total sequence of all monomer units. In such a copolymer with branches and more properties of interest, the information would increase.

However, all this characterizes just one single molecule, since not only the chain lengths are distributed in a polymer but also the other properties of interest.

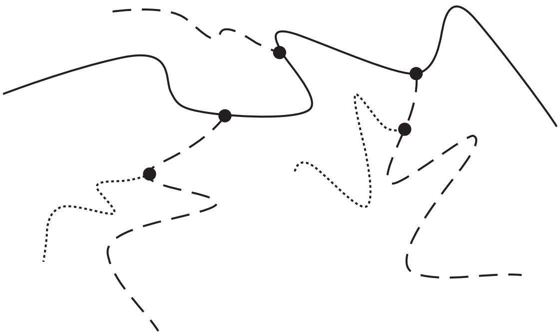

Figure 1.8 Schematic topology of a branched macromolecule with backbone chain, branches, and branches on branches. The overall chain length of the molecule is given by the total number of monomers in all branches.

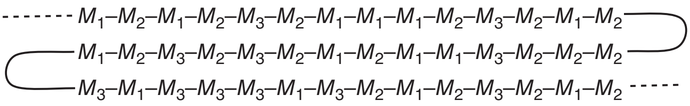

Figure 1.9 Schematic monomer distribution in an example terpolymer chain.

In order to get a usable description of our mole of chains, we have to sort them with respect to certain criteria.

For example, we can count only for the number of branches and put all chains with identical branching numbers into one “box.” Depending on the reaction system, we will end up with a few boxes only (if branching is not frequent) or many of them. In each box, we will have chains of very different lengths again and we can also put them into smaller “sub-boxes.” Thus, we obtain numbers as $n(s, j)$ denoting the number of chains in a sub-box having j branches and chain length s. We can also revert to the sort process and start with boxes for the chain length. This seems to be more practical, since we expect many different chain lengths, and thus many boxes on the first level of sorting. We could also refine the sorting by using sub-sub-boxes for the lengths of the branches – or we better save them by not taking care of branches at all and put all chains with the same lengths into one box.

Nevertheless, whatever we use as sorting criterion, when we run our reaction again under exactly the same conditions (mixture, temperature, pressure, etc.) and perform our sorting again, we will note that the second experiment leads to different content, that is, numbers of chains, in our boxes. And the next attempt will be different again, and so on. After thousands of experiments, we will get a feeling of how the contents of the boxes are distributed *in average* and what kind of variations we can expect. We will learn that the probability that our process leads to exactly n chains with length s and j branches is not 1, but given by a distribution, too. This distribution must not be mixed up with the distribution describing the basic properties, for example, the chain-length or molecular-weight distribution. The chain-length distribution summarizes molecules of type P_s. In addition, for each single s we will have different values for different experiments or stochastic realizations, respectively.

We will illustrate this important and general structure with a very simple example.

1.4.1 Chemical Master Equations

Assume that we are interested in the number $n_A(t)$ of a single type of molecules A having very low initial number n_0 in a small reactor, for example, an initiator which reacts in the following reaction R to a product which is no longer of interest to us.

$$R : A \xrightarrow{k} \emptyset \tag{1.24}$$

Basically, the reaction (1.24) has to be understood as a *stochastic process*: In a certain time interval, the reaction may happen – or it may not. This holds for all further time intervals and therefore – due to the randomness of the reaction – after a while we will find still n_0 molecules (depending on the value of k this might be not probable, but possible), or zero molecules or (most probably) something in between. Thus, if the system is initialized with n_0 molecules we can only discuss the probability that there are $n_A(t) = x$ molecules present at time t.

This is pictured in Figure 1.10. We consider a system with a number of initial molecules. After regular time intervals we count again and thus know whether the reaction took place meanwhile. Starting with seven molecules, after each time interval (reaction happened (indicated by an arrow) or did not happen (indicated by a line with bullet end)) we get a new status of the total number. If we repeat the experiment, we may end up with a different state reached through a different path.

If we repeat this very often, we will expect to get a distribution of numbers for the final state. Its related average number could even be a non-integer value, for example, 5.5. Based on this average, one could define a heuristic formula like $n_A(t) = n_0 exp(-kt)$ and use this as a description for the reaction independent of its stochastic character.

For a formal description of (1.24), we define a (discrete) random variable $X_A(t)$ describing the number of molecules of species A at time t. The reaction probability for reaction R is specified by the so-called *propensity function* $a_R = a_R(X_A(t), t)$, which is equal to the product of a rate constant k and the number of possible combinations of reactant molecules involved in reaction R (see [6]). Thus, the propensity of reaction (1.24) is given by $a_R = kX_A(t)$. Note that this is really a discrete process; the possible number of molecules is an integer value.

Returning to (1.24) and the underlying stochastic process, we define the probability distribution function (PDF) of the random variable $X_A(t)$ by

$$p(t, x) = P[X_A(t) = x], x \in N \tag{1.25}$$

It describes the probability that at time t we have x molecules of type A. Its time evolution is given by the *CME*:

$$\begin{aligned}\frac{dp(t,x)}{dt} &= a_R(x+1,t)p(t,x+1) - a_R(x,t)p(t,x)\\ &= k(x+1)p(t,x+1) - kxp(t,x)\end{aligned} \tag{1.26}$$

In general, the description using a CME governs infinite many system realizations and describes how the probability changes for single realizations. Here, the time derivative of $p(t, x)$ for a given x depends on the probability of systems $p(t, x + 1)$

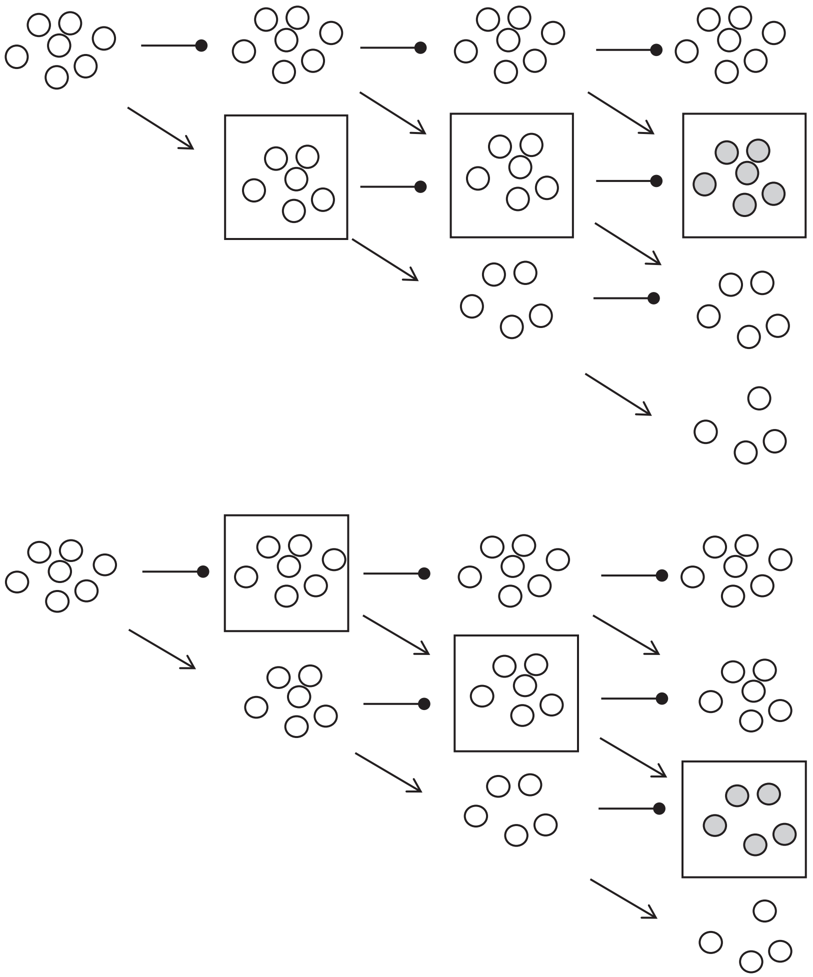

Figure 1.10 Two possible paths for the number of molecules disappearing with a certain rate. In the first picture, the status of the system is 7 at time 0, then 6 at time 1, then still 6 at times 2 and 3 (7–6–6–6). This means that in only one of the three time intervals the reactions really happened. For the second path, the reaction takes place in the second and third time step, leading to status 7–7–6–5 at times 0–1–2–3. The difference is simply given by the underlying stochastic process. In order to get a reasonable average, one has to repeat this very often.

having just one more molecule. For reaction schemes with M reactions, the general CME reads

$$\frac{dp(t,x)}{dt} = \sum_{m=1}^{M} [a_m(x - v_m, t)p(t, x - v_m) - a_m(x, t)p(t, x)] \tag{1.27}$$

where v_m is the stoichiometric factor of the species in reaction m. For our simple case and for moderate numbers of A, a numerical solution of (1.26) is possible and some results are presented in Figure 1.11.

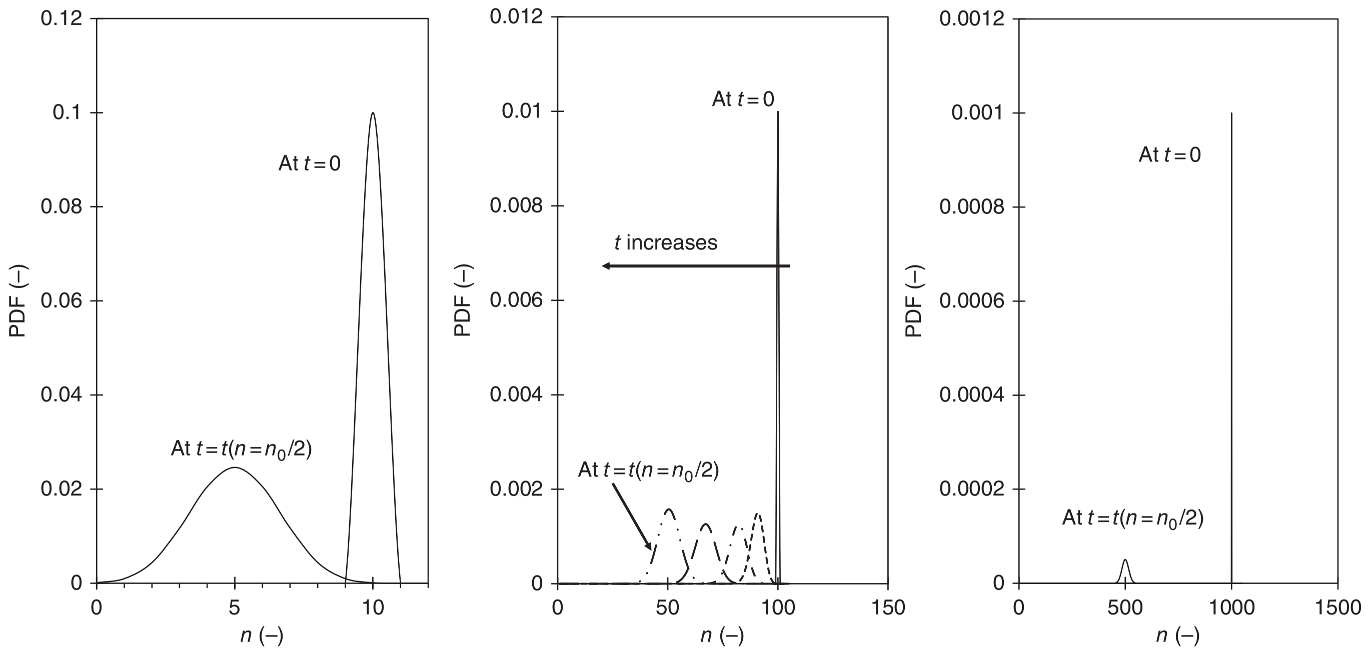

Figure 1.11 Time evolution of PDF of $X_A(t)$ for $n_0 = 10(a), 100(b), 1000(c)$ until the average reaches $n_0/2$. The PDF presents the probability that there are n molecules (x-axis) present in the system at time t. In the beginning we have $p(0, n_0) = 1$, then the PDF broadens and moves from right to left.

We can observe that the lower the initial number n_0, the more important is the distribution and its standard deviations compared to the average number. This is very important, since the reaction R considered earlier consists only of one single molecule type – and we already had to solve a CME with 10, 100, and even 1000 equations. For reactions between two different molecules, this number of equations is squared; and for a polymerization system with species $P_1, P_2, \dots, P_s$ for very large s, the CME reaches a tremendous dimension which will not be solved as a set of differential equations for some time in future.

Fortunately, the complexity can be reduced drastically if certain molecules or properties appear "very often" in a system, that is, if they have many "copies." Then we talk of the so-called *high copy numbers* in the stochastic description of chemical reactions. The higher the copy number, the less important is the knowledge of the full PDF, see Figure 1.11; case $n_0 = 1000$ and the PDF can be replaced by its average without too much loss of information. Generally, this reduction is not trivial, but for the single reaction (1.26) we can do this. Introducing the moments

$$\lambda_0(t) = \sum_{x=0}^{\infty} p(t,x),\ \lambda_1(t) = \sum_{x=0}^{\infty} xp(t,x) \tag{1.28}$$

and inserting them into (1.26), we can derive the following differential equation for the average $A(t) = \lambda_1(t)/\lambda_0(t)$:

$$\frac{dA(t)}{dt} = -kA(t) \tag{1.29}$$

It is no surprise that this is the well-known RKE belonging to reaction (1.24). The time evolution of the RKE describes the average of the PDF from the CME that is associated with the stochastic process. In Figure 1.12, we have sketched our procedure. The reaction system leads to a CME resulting in the PDF. We can *average the PDF* to obtain values of interest, but also *average the CME* to an RKE and then compute the required values directly. If possible, we want to use the path via the RKE – complex enough for polymerization - since it is much easier to derive and to solve than the general CME.

In order to perform the step from CME to RKE, we have to ask what the high and low copy numbers are in this context. For example, in radical polymerization we sometimes have to consider concentrations of radicals at a level of 10^{-10} mol/l. Assume a very small reactor with a volume of only 1 cm^3. Then we have about 6×10^{10} radical molecules, which is a very high copy number. If we distinguish those polymer radicals by their chain lengths and assume a maximum chain length of $s = 10^5$, we still have an average of 10^5 molecules per species class P_s. In

$$\begin{tikzcd}
\boxed{\text{Reaction}} \arrow[r] & \boxed{\text{CME}} \arrow[r] \arrow[d] & \boxed{\text{PDF}} \arrow[d] \\
& \boxed{\text{RKE}} \arrow[r] & \boxed{A(t)}
\end{tikzcd}$$

Figure 1.12 Commutative diagram for CME and RKE. Note that the upper path usually cannot be performed with high accuracy, since the CME cannot be solved directly.

addition, characterizing the polymers by the number of branches and assuming a maximum of about 10–100 branches per chain, we still will be on the safe side with about 10^3–10^4 chains per box. For further classification, for example, also distinguishing with respect to the lengths of branches, it may happen that there are no two chains with identical properties. An illustrative example for a rather simple system is given in (1.23). Then the PDF becomes important, since it may deviate much from the average.

In view of this consideration, we can state that for chain-length distributions and their typical concentration ranges and properties, we usually have "enough" molecules to replace the CME by an RKE. However, we will encounter the CME again in Section 4.3.3 on emulsion polymerization, where we will meet really low copy numbers of radicals.

1.4.2 Approaches to Polymer Properties

Coming back to the description of a polymer and its characteristics we can generally describe a polymer molecule by

$$P_{s,j_1,j_2,\dots,j_k,\dots} \tag{1.30}$$

where s denotes the chain length and the j_k an open number of additional properties. We have learned in Section 1.4.1 that by introduction of too many further properties we reduce the copy number of one particular kind of molecule to a region were the treatment of a CME is necessary. Imagine how many polymer chains of length 1538 with 12 branches, all of given length, 189 comonomer units, 67 of them with a dangling end group, are really in a reactor even if, in principle, all phenomena to generate such chains are present. With Equation (1.23) we have shown already on the inner composition of copolymers how small the probability for one special structure of a polymer molecule can be.

Therefore, it makes sense to reduce the number of observed properties right from the beginning. The selection and the level of details depend on what may happen in a reactor, what can be measured or controlled, and so on. This will often lead to only a few additional properties of interest and sometimes it is sufficient to know them as an average over the whole polymer. For that we can sum with respect to all additional indexes j_k and define

$$P_s := \sum_{j_1} \sum_{j_2} \sum_{\cdots} P_{s,j_1,j_2,\dots} \tag{1.31}$$

This means that the polymer P_s as defined in Definition 1 can be now considered as a description of a complex polymer chain reduced to its main property, the chain length s. Obviously, we may leave out one or more of the summations in (1.31) and keep some properties in the description, for example,

$$P_{s,j_1} := \sum_{j_2} \sum_{\cdots} P_{s,j_1,j_2,\dots} \tag{1.32}$$

In terms of our picture of putting chains into boxes used in the beginning of this section, (1.31) means that we only have boxes for chains with different polymer degree s, where for (1.32) we introduce sub-boxes for just one additional property. The general description with all indexes would imply more and more sub-sub-sub-boxes with less and less single chains.

An alternative to reduce boxes is to use a summation with respect to chain length s and all other indexes, where we multiply by some index:

$$C_1 := \sum_s \sum_{j_1} \sum_{j_2} \sum_{\cdots} \boxed{j_1} \cdot P_{s,j_1,j_2,\ldots} \tag{1.33}$$

In order to better show what this means we can also use (1.32) and write

$$C_1 = \sum_s \sum_{j_1} j_1 \cdot P_{s,j_1} \tag{1.34}$$

C_1 is nothing else than the total number of property j_1 in all polymer chains, that is, independent of their chain length. We are not introducing sub-boxes for the property j_1, but we throw a coin into one collector box aside whenever we see this property on a chain. Such a global counter is quite helpful in the description of polymer kinetics, and is widely used if the (averaged) property does not differ too much from chain to chain. For example, the incorporation of a comonomer can often be described nicely using a counter. It is also possible to introduce a chain-length-dependent counter for j_1 by not summing over the index s in (1.34).

$$C_{s,1} = \sum_{j_1} j_1 \cdot P_{s,j_1} \tag{1.35}$$

In terms of our boxes, this implies that we have one counter box for each chain-length box. However, in contrast, to use detailed sub-boxes for property j_1, the counter boxes will fill up much quicker; in most cases, they will belong to a high copy number, even in this chain-length-dependent case. While global counters can very easily be added to reaction kinetics, chain-length-dependent counters require more mathematical preparations. We sketch this in Section 2.6.4.

For the derivation of reaction kinetics and its equations in Chapter 2, we will use the full average (1.31) and global counters for all properties of interest. Due to the character of the summation process, a global counter for a certain property can usually be treated like a virtual reaction product without mass.

1.4.3 Stochastic and Deterministic Simulation

We have shown that the CME describes a stochastic process, but its solution (e.g., (1.26) at least) could be obtained by the deterministic solution of some differential equations. In literature, deterministic (using differential equations) and stochastic (using so-called Monte Carlo methods) approaches to polymer reaction kinetics are often separated. After the discussion in this section, we are now able to explain the role of these approaches.

The CME is a highly dimensional equation for a highly multivariate distribution. Its solution is deterministic, a multivariate probability function as we have presented in Figure 1.11. The problem is that in nearly all cases of interest (and in particular for polymer kinetics) the CME cannot be solved directly as we have done for the simple case. Instead, one can try to use a stochastic algorithm to generate *single realizations* of the stochastic process behind the CME. In order to give an idea of how this works, we consider the simple reaction (1.24) again.

Starting with a given number of molecules A, we can set a reasonable time interval. From the propensity function we know a rate of reaction. Then we perform a random experiment to decide whether the reaction really happens in the given time interval. We update the number of molecules accordingly, choose the next time interval, and repeat the random experiment. This is already pictured in Figure 1.10. Reaching a given end time, we will end up with one single number of molecules that can be considered as one realization of the CME (1.26).

Does it make sense to compare this single value to a real experiment? Of course, not, since the experiment is also one realization of the process and the results could differ quite a lot. Even for high copy numbers, we cannot expect the one single realization of the CME to be especially close to the average. Therefore, we have to repeat the whole procedure very often, until we can estimate that the obtained average of results is reliable. This is a Monte Carlo method and – neglecting all details – is well known as the stochastic simulation algorithm (SSA) [6]. We have seen that by this algorithm we obtain an approximation of the PDF and its quality depends on how often we repeat the stochastic process. Actually, this quality is mostly oriented on the accuracy of the average of the PDF, even if we also obtain information on the distribution itself. In practice, one has to run thousands up to millions of single runs to get a relatively smooth result without too much of perturbations. For polymer systems, one can incorporate many properties (see Figures 1.8 and 1.9), but still one has to average them for further treatment and comparison. The price to be paid for this flexibility is the computational effort and the relatively low accuracy compared to the exact solution of the CME.

Note: *The Monte Carlo method approximates the solution of the CME in a stochastic way. It is based on the propensities given in the CME and not on the RKE. In principle, the CME could also be solved by a differential equation solver, but the Monte Carlo method is the method of choice for CMEs.*

The formal reduction of a CME to an RKE is not trivial, but can be very complex. It also requires assumption on the stochastic coupling between variables. Therefore, it is quite common to derive the RKE directly from the reaction system using reaction rates. The RKE describes the averages of the PDF. We remember again that these averages are not those we have taken with respect to polymer properties (1.31), but the averages of the stochastic process.

Note: *The RKE is an approximation of the underlying CME assuming high copy numbers. It is solved by analytical (in rare cases) or numerical methods for differential algebraic equations. It is not solved by a Monte Carlo method. The RKE may also describe a number of property variables increasing the dimension of the system. However, realistic dimensions for a numerical treatment are only 1 (already used for the chain length), 2, or 3.*

The two approaches are illustrated in Figure 1.13

The two results $A_R(t)$ and $A_C(t)$ of the different approaches (both expressions representing all state variables of a system) are not identical. Common parts are usually more accurately given by the solution $A_R(t)$ of the RKE, whereas $A_C(t)$ might include more properties. Computing times to get $A_R(t)$ can often be seconds or minutes; for $A_C(t)$ it may sometimes be hours or even days. Moreover, the

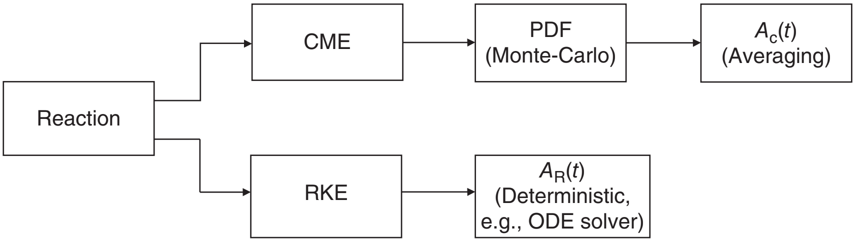

Figure 1.13 Diagram for CME and RKE including methods.

accuracy control is more difficult for Monte Carlo methods. We can also mention that there are mixed or hybrid approaches in use combining the stochastic solution of the CME with the deterministic solution of the RKE [7, 8].

Since the main property for polymers still is the chain length and the RKE for chain-length distributions can directly be solved, in this book we mainly derive, analyze and solve RKEs. Reaction phenomena will directly be transformed into differential equations, as done in major parts of the literature. If we want to consider additional properties, we will decide about the copy number and use a reasonable approach, sometimes global counters, sometimes higher dimensional RKEs, sometimes stochastic approaches. Last but not the least, the taken approach has to be oriented to the capabilities of the measurement techniques of Table 1.2, for example, whether they are based on averages or full distributions.