

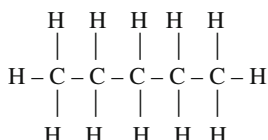
## Chapter 2

# Physical Structure of Macromolecules

In this chapter, the structure of single macromolecules is discussed, together with the possibilities for their internal motion. This leads to the concept of the shape and extension of macromolecules as calculated by random walk statistics, in theta solution, in bulk and in the melt. The chapter further contains the description of molar mass and molar mass distribution.

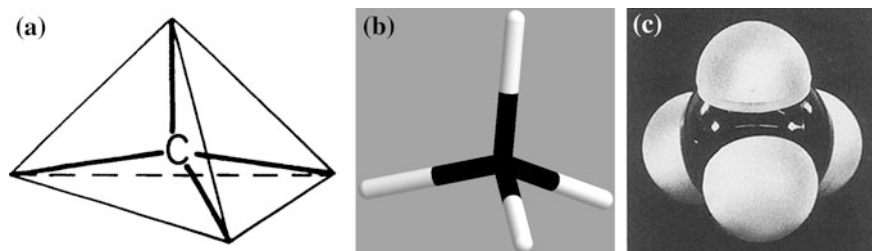
### 2.1 Structure and Brownian Motion of Macromolecules

Let us consider the spatial shape of a molecule consisting of five consecutive carbon atoms, i.e., of a pentane or a substituted pentane. The structural formula of pentane



suggests an incorrect picture of the spatial shape of the molecule. In reality, the four bonds of a carbon atom can never be situated in the same plane; neither will the single bonds between successive carbon atoms form parts of the same straight line. The four single bonds of a carbon atom build up a regular tetraeder, as illustrated in part a of Fig. 2.1.

With the carbon atom in its center, the bonds point to the vertices of the tetraeder. The spatial angle between each pair of bonds has the same fixed value of  $\vartheta = 109.47^\circ$  ( $\cos \vartheta = -1/3$ ). In Fig. 2.1, this structure is further illustrated by two models of the methane molecule. The “Buechi-model” places emphasis on the direction of the bonds, which are indicated by small tubes. This model allows the illustration of the change of the spatial shape of a molecule by the rotation around single carbon-carbon bonds (the *conformational changes of the molecule*). The



**Fig. 2.1** **a** The directions of the four single bonds extending from a carbon atom **b** Buechi-model of the methane molecule **c** Stuart-model of the methane molecule. Reprinted from [1]

“*Stuart-model*” visualizes the occupation of space of a molecule by its outer electron shells. The dimensions of Stuart models are mostly in proportion to the real molecule (scale  $1:10^8$ ).

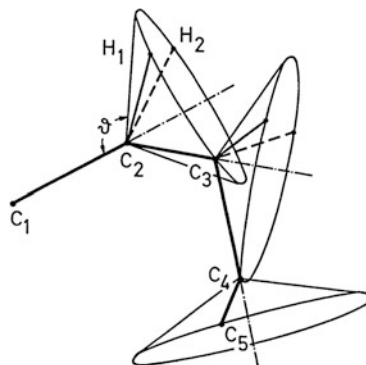
Next, we discuss the spatial shape and the conformations of the pentane molecule as illustrated in Fig. 2.2. The direction of the first carbon-carbon bond ( $C_1-C_2$ ) is assumed to be fixed. On rotation around this bond, the three further bonds starting from atom  $C_2$  will move on the surface of a cone with a generating line, including the angle  $\vartheta$  with the direction of the first bond. The next carbon atom  $C_3$  will then be situated anywhere on the basic circle of this cone. Fixing the position of  $C_3$  for the moment, the fourth carbon atom  $C_4$  will move on the basic circle of a cone with a generating line including the angle  $\vartheta$  with the direction ( $C_2-C_3$ ), and so on.

If all rotations around the bonds  $C_1-C_2$ ,  $C_2-C_3$ ,  $C_3-C_4$  can take place independently of each other, the last carbon atom  $C_5$  can reach a large number of spatial positions, even if the position of  $C_1$  and the direction of ( $C_1-C_2$ ) are kept fixed. The change in shape of the pentane molecule occurring in this manner looks similar to the twisting of a worm and is called the “*micro-Brownian motion*” of the macromolecule.

The micro-Brownian motion of the macromolecule is the conformational change in shape of the molecule originating from the rotations around the single C–C bonds of the main chain.

By the continuous micro-Brownian motion originating from the thermally induced kicks of the environment, a macromolecule will pass through all its conformations permitted by the positions of its neighbors. Most conformations will lead to the shape of a coil. A few conformations will adapt the shape of a stretched ellipsoid, only one will lead to the *completely stretched conformation*. Consequently, we expect the macromolecule averaged over time to assume the *shape of*

**Fig. 2.2** Conformations of the pentane molecule

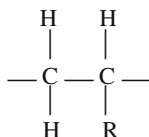


a coil, whose details will continuously change with time. Description and calculation of these coils will be handled in Sect. 2.3.

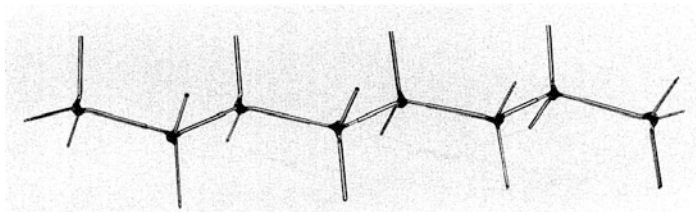
The *completely stretched conformation* is defined by the condition that the distance between the beginning and the end of the molecule is maximal. In Fig. 2.3, the carbon chain with single bonds is shown in its completely stretched conformation in the representation of a Buechi-model.

In this conformation, all bonds of the main chain are situated in one single (horizontal) plane in the shape of a “zick-zack”. The other two bonds of the carbon atoms emerge from this plane, one into the direction upwards and one into the direction downwards.

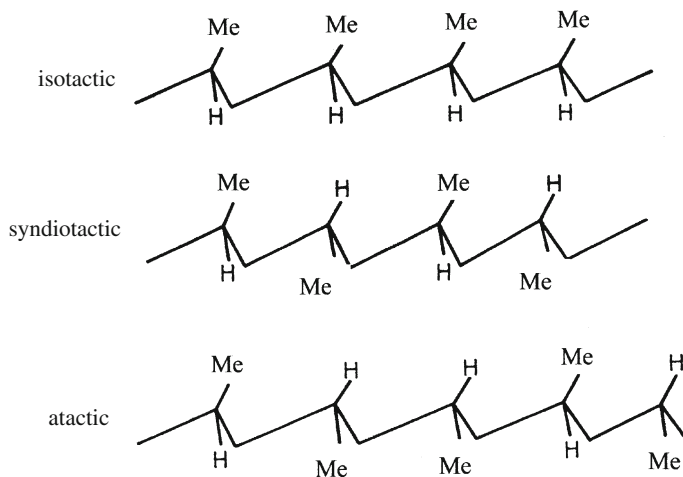
The completely stretched conformation is well suited to introduce the concept of *tacticity of vinyl-polymers*. The class of vinyl-polymers is characterized by a structural unit of the following type



with  $R$  being an arbitrary side-group different from  $H$ . The spatial placement of the side groups  $R$  plays an important role for the properties of the vinyl-polymer. This is illustrated for the case of poly(propylene) PP ( $R = \text{Me} \equiv \text{CH}_3$ ) in Fig. 2.4.



**Fig. 2.3** Buechi-model of a carbon chain in the completely stretched conformation



**Fig. 2.4** Illustrating the tacticity of poly(propylene)

Consider the completely stretched conformation of the PP-chain. If all methyl-groups are situated on the same side of the principle plane, the polymer is called *isotactic*. If the methyl-groups are alternatively situated above and below the main plane, the polymer is called *syndiotactic*. If the position of the methyl-groups is irregular, the polymer is called *atactic*. Isotactic and syndiotactic polymers tend to *crystallization*, because their molecules fit better into the crystal lattice. Stereo-specific polymers are obtained by special coordination polymerization methods with mixed catalysts (Ziegler and Natta).

## 2.2 Molar Mass and Molar Mass Distribution

Next, we deal with the molar mass of the macromolecules, which is a very important characteristic property of polymers. The definition of the *molar mass* (sometimes also called molecular weight) is reasonable only for *uncrosslinked* polymers. For *uncrosslinked, not branched homopolymers*, the molar mass characterizes the structure of the molecule, apart from its tacticity. For *uncrosslinked, branched homopolymers*, this information has to be supplemented by the number, length and the topology of the branches.

We start with the definition of *Avogadro's number*. This number does not have a physical dimension, but a unit is designated to it, called  $\text{mol}^{-1}$ , meaning "per mol".

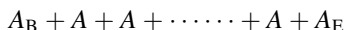
$$N_A = 6.0225 \cdot 10^{23} \text{ mol}^{-1} \quad (2.1)$$

The mol is used as a unit of the amount of a material. The totality of  $N_A$  identical items is designated as one mol of those items. Let  $m$  be the mass of a molecule (in kg), then its molar mass is defined as

$$M = N_A \cdot m \quad (2.2)$$

The unit of the molar mass is kg/mol. The number  $N_A$  is defined in such a way that the molar mass of the nuclide  $^{12}\text{C}$  becomes exactly  $0.012 \text{ kg/mol} = 12 \text{ g/mol}$ .

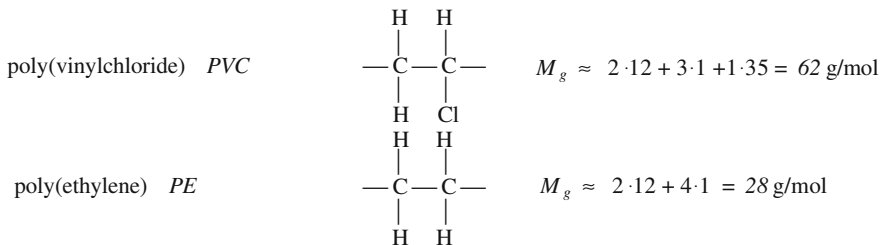
Consider the molecule of a non-crosslinked, unbranched homopolymer:



The moieties  $A_B$  and  $A_E$  of the beginning and the end of the molecule respectively, will generally differ from its center part, which consists of  $P$  repetitions of one single group  $A$ .  $P$  is called the *degree of polymerization*; the repeating unit  $A$  is called the *structural unit*. If  $M_g$ ,  $M_B$ , and  $M_E$  are the molar masses of the structural unit, the beginning and the end moiety of the molecule, respectively, the molar mass of the complete molecule is

$$M = M_B + P \cdot M_g + M_E \approx P \cdot M_g \quad (2.3)$$

The last part of this equation is valid approximately at sufficiently large values of  $P$ . Some examples are:



As  $P$  has to be an integer, the molar mass can only assume a finite number of discrete values, which are, apart from the small term  $M_B + M_E$ , multiples of  $M_g$ .

We describe the distribution of the molar mass by either *counting* or *weighing* the molecules with a certain molar mass and arrive at a scheme like that of Table 2.1, in which the  $k$  classes are arranged in increasing order of their degree of polymerization, i.e.,  $P_i < P_{i+1}$  for  $i = 1$  to  $k - 1$ . Let  $n_i$  be the number of molecules with molar mass  $M_i$  and let us use the abbreviation:

$$m_i = n_i M_i \quad (2.4)$$

**Table 2.1** Discrete values for the distribution of the molar mass arranged in  $k$  classes

Number of molecules	Degree of polymerization	Molar mass	Mass of the fraction
$n_1$	$P_1$	$M_1 \approx P_1 M_g$	$W_1 = n_1 M_1 / N_A$
$n_2$	$P_2$	$M_2 \approx P_2 M_g$	$W_2 = n_2 M_2 / N_A$
.....			
$n_k$	$P_k$	$M_k \approx P_k M_g$	$W_k = n_k M_k / N_A$

The *mass* of the *fraction*  $i$ ,  $W_i$ , is given by the equation

$$W_i \approx n_i M_i / N_A = m_i / N_A \quad (2.5)$$

We further define the total number  $n_0$  of the molecules considered, by

$$n_0 = \sum_{i=1}^k n_i \quad (2.6)$$

and the *number distribution function* of the molar mass,  $f(M_i)$ , as the *relative number* of molecules with a molar mass equal to  $M_i$ .

$$f(M_i) = n_i / n_0 \quad (2.7)$$

The number distribution function obeys the normalization condition

$$\sum_{i=1}^k f(M_i) = 1 \quad (2.8)$$

and constitutes a *discrete distribution function*, i.e., it is not defined for values  $M \neq M_i$ . In addition, we define the *mass distribution function* of the molar mass,  $h(M_i)$ , as the *relative mass* of molecules with a molar mass equal to  $M_i$ :

$$h(M_i) = \frac{W_i}{\sum_{i=1}^k W_i} = \frac{n_i M_i}{\sum_{i=1}^k n_i M_i} = \frac{m_i}{\sum_{i=1}^k m_i} \quad (2.9)$$

which, of course, is also normalized

$$\sum_{i=1}^k h(M_i) = 1 \quad (2.10)$$

and also constitutes a discrete distribution function.

For mathematical descriptions, it is often necessary to change from the *discrete distribution function*  $f(M_i)$  to a *continuous distribution function*, which is defined for all values of the molar mass. This is achieved in two steps:

Step 1: We extend the range of definition of the distribution function to all values of the molar mass. Around each point  $M_i$  of the  $M$ -axis, an interval  $[B_i, B_{i+1})$  is created, which starts from the midpoint between  $M_{i-1}$  and  $M_i$ ,  $B_i = (M_{i-1} + M_i)/2$  and ends at the midpoint between  $M_i$  and  $M_{i+1}$ ,  $B_{i+1} = (M_i + M_{i+1})/2$ . For the first interval we choose the bounds  $B_1 = M_1 - M_g$  and  $B_2$ , for the last interval the bounds  $B_k$  and  $B_{k+1} = M_k + M_g$ . The *widths*  $b_i$  of those intervals are

$$\begin{aligned} b_i &= B_{i+1} - B_i = (M_{i+1} - M_{i-1})/2 & \text{for } i &= 2 \text{ to } k-1 \\ b_1 &= M_g + (M_2 - M_1)/2 & \text{and } b_k &= M_g + (M_k - M_{k-1})/2 \end{aligned} \quad (2.11)$$

As  $f(M)$  is defined as the relative number of molecules with a molar mass within the interval  $[B_i, B_{i+1})$ , we put  $f(M) = f(M_i)$  for  $B_i \leq M < B_{i+1}$ .  $f(M)$  is the probability to find a molecule within the interval  $[B_i, B_{i+1})$ . If the molar masses would be equally distributed within this interval,  $f(M)dM/b_i$  would be the probability to find a molecule with a molar mass between  $M$  and  $M + dM$  within this interval. Consequently, we define a new distribution function

$$g(M) = f(M_i)/b_i \quad \text{for } B_i \leq M < B_{i+1} \quad (2.12)$$

$g(M)$  is a step function defined for all values of  $M$  with discontinuities at the points  $B_i$ .  $g(M)dM$  is the probability to find a molecule with a molar mass between  $M$  and  $M + dM$  in the interval  $[B_i, B_{i+1})$ .

Step 2: Generally, the number of classes  $k$  will be sufficiently large to replace this step function by a continuous function  $g(M)$  which will be approximately equal to  $f(M_i)/b_i$  at the points  $M = B_i$  and is smooth in between. To distinguish between  $f(M)$  and  $g(M)$ , we will call the latter the *number distribution density* of the *molar mass*. The function  $g(M)dM$  describes the *relative number* of molecules with a molar mass between  $M$  and  $M + dM$ . It will occur in all integral representations of the molar mass. Its condition of normalization reads

$$\int_0^{\infty} g(M)dM = \sum_{i=1}^k \int_{B_i}^{B_{i+1}} g(M)dM \cong \sum_i b_i g(M_i) = \sum_i f(M_i) = 1 \quad (2.13)$$

Besides the number distribution density, an other distribution function is introduced, the *mass distribution density*, which describes the *relative mass* of the molecules with a molar mass between  $M$  and  $M + dM$ :

$$w(M) = M \cdot g(M)/M_n \quad (2.14)$$

with

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum m_i}{\sum (m_i/M_i)} = \frac{\sum m_i}{\sum n_i} \quad (2.15)$$

The denominator  $M_n$  is introduced to normalize the mass distribution density by the condition:

$$\int_0^{\infty} w(M) dM = \frac{1}{M_n} \int_0^{\infty} M g(M) dM = 1 \quad (2.16)$$

or

$$M_n = \int_0^{\infty} M g(M) dM \quad (2.15')$$

Apart from one case, the usual methods for the determination of the molar mass, do not yield the entire distribution function, but only certain averages of it. The most important are

$M_n$     *number average* of the molar mass  
 $M_w$     *weight average* of the molar mass  
 $M_z$     *z-average* of the molar mass  
 $M_v$     *viscosity average* of the molar mass

The *number average*  $M_n$  is the mean value of  $M$  calculated by using the number distribution of the molar mass and was defined in Eqs. (2.15) and (2.15'). The *weight average*  $M_w$  is the mean value of  $M$  calculated by using the mass distribution of the molar mass and is defined by

$$M_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (2.17)$$

and

$$M_w = \int_0^{\infty} M \cdot w(M) dM = \frac{1}{M_n} \cdot \int_0^{\infty} M^2 g(M) dM \quad (2.17')$$



The second part of Eq. (2.17') is found by multiplying Eq. (2.14) with  $M$  and integrating over  $M$ . The  $z$ -average  $M_z$  is the ratio of the number average of  $M^3$  to the number average of  $M^2$ :

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum m_i M_i^2}{\sum m_i M_i} \quad (2.18)$$

and

$$M_z = \frac{\int_0^\infty M^3 \cdot g(M) dM}{\int_0^\infty M^2 \cdot g(M) dM} \quad (2.18')$$

Finally, the  $a$ th power of the *viscosity average*  $M_v$  is defined as the mass average of  $M^a$ .  $a$  is a number between 0 and 1, whose value depends on the choice of the system (polymer—solvent) and on the temperature (Compare also Sect. 2.4).

$$M_v = \left[ \frac{\sum m_i M_i^a}{\sum m_i} \right]^{1/a} = \left[ \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a} \quad (2.19)$$

and

$$M_v = \left[ \int_0^\infty M^a \cdot w(M) dM \right]^{1/a} \quad (2.19')$$

If and only if, the polymer is *monodisperse*, ( $n_1 = n_2 = n_{i-1} = n_{i+1} = \dots = n_k = 0$ ;  $n_i = n_0$ ), all averages of the molar mass will be equal and equal to  $M_i$ . For a *polydisperse* polymer the following equation always holds

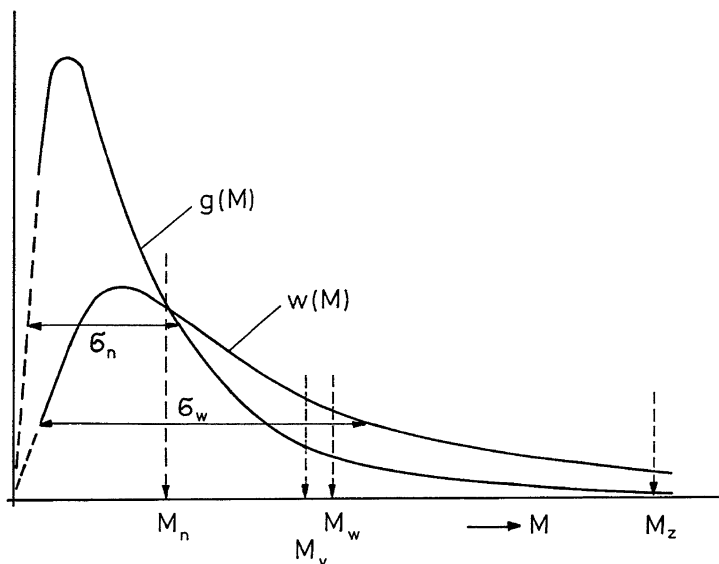
$$M_n < M_v \leq M_w < M_z \quad (2.20)$$

$M_v$  is found between  $M_n$  and  $M_w$ , generally closer to  $M_w$ . The equality  $M_v = M_w$  only holds in the (rare) special case  $a = 1$ . Equation (2.20) is not only an experimental fact, but a mathematical consequence of the definitions of the various averages.

The ratios  $M_w/M_n$  and  $M_z/M_w$  increase with increasing width of the molar mass distribution. Hence,

$$U \equiv \frac{M_w}{M_n} - 1 \geq 0 \quad (2.21)$$

and



**Fig. 2.5** Distribution densities of the molar mass of a technical polymer and the positions of its averages

$$\tilde{U} \equiv \frac{M_z}{M_w} - 1 \geq 0 \quad (2.22)$$

are introduced as measures for the width of the molar mass distribution.  $U$  is called the *nonuniformity of Schulz*,  $U + 1 = M_w/M_n$  the *polydispersity factor*.

Figure 2.5 shows a schematic drawing of the *number distribution density*  $g(M)$ , the *mass distribution density*  $w(M)$  and the positions of the molar mass averages for a technical polymer. Plotted over a linear scale of the molar mass as abscissa, those distribution densities are mostly strongly asymmetric curves with a long tail at the high molar masses. Their values at low molar masses are often difficult to determine, and are, therefore, indicated by dashed lines. According to Eq. (2.14)  $w(M)$  is shifted to higher molar masses with respect to  $g(M)$ . Both curves intersect at the abscissa  $M = M_n$ . The line of gravity of the density function  $g(M)$  passes through  $M_n$ , the line of gravity of the density function  $w(M)$  passes through  $M_w$ . The standard deviations of the curves  $g(M)$  and  $w(M)$  are indicated by  $\sigma_n$  and  $\sigma_w$ . The maximum of the curve  $g(M)$  is situated left to the maximum of the curve  $w(M)$  and both are situated left to the value of  $M_n$ .

The averages may be interpreted as statistical parameters of the distribution densities  $g(M)$  and  $w(M)$ . If the stochastic quantity  $M$  is distributed with the density  $g(M)$ , its mean value is equal to  $M_n$  and its variance is given by

**Table 2.2** Parameters of the molar mass distribution of some technical polymers ( $M$  in kg/mol)

Polymer	$M_n$	$M_w$	$M_z$	$M_w/M_n$	$M_z/M_w$	Lit.
Poly(styrene) PS N 7000	182	385	771	2.12	2.00	[2]
Poly(styrene) Styron 666	120	250	–	2.08	–	[3]
Poly(styrene) PS 158 K	120	278	–	2.30	–	[4]
Poly(vinyl chloride) Solvic	38.6	84	154	2.18	1.83	[5]
Poly(methyl methacrylate) Plexiglas 7 N	60	95	–	1.6	–	[6]
Poly(ethylene) HDPE HE 6914	17.6	284	2430	16	8.6	[7]
Poly(ethylene) LDPE Lupolen 1840 H	15.5	258	2740	16.6	10.6	[7]
Poly(propylene) Moplen HP 501 N	42.3	254	–	6.0	–	[8]
Poly(carbonate) PC1	15	30	–	2.0	–	[4]

$$\sigma_n^2 = \int_0^{\infty} (M - M_n)^2 g(M) dM = M_w M_n - M_n^2 = U M_n^2 \quad (2.23)$$

If the stochastic quantity  $M$  is distributed with the density  $w(M)$ , its mean value is equal to  $M_w$  and its variance is given by the equation

$$\sigma_w^2 = \int_0^{\infty} (M - M_w)^2 w(M) dM = M_z M_w - M_w^2 = \tilde{U} M_w^2 \quad (2.24)$$

$\sigma_n$  and  $\sigma_w$  are the *standard deviations* of the distribution densities  $g(M)$  and  $w(M)$ , respectively. The quotient of standard deviation to mean value is known in statistics as the *variation coefficient*  $c$  and constitutes a measure for the relative width of the distribution density. From (2.23) and (2.24) we obtain the statistical meaning of the polydispersities as the corresponding squares of the variation coefficients

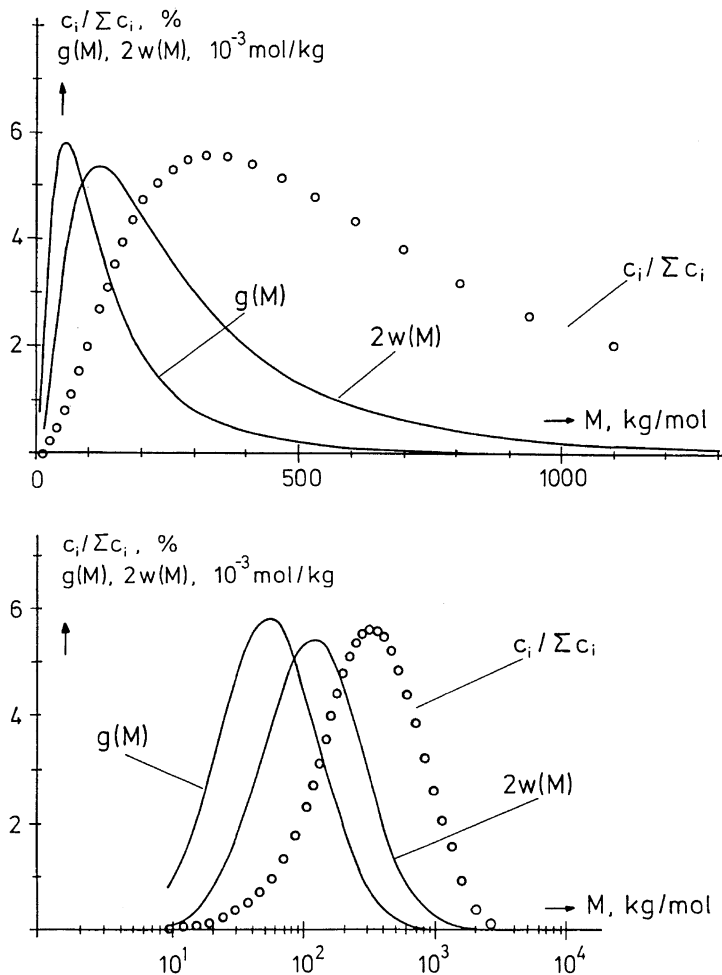
$$U = \frac{\sigma_n^2}{M_n^2} = c_n^2 \quad (2.25)$$

and

$$\tilde{U} = \frac{\sigma_w^2}{M_w^2} = c_w^2 \quad (2.26)$$

Equations (2.23) and (2.24) also prove the general validity of Eq. (2.20). The left-hand side of Eq. (2.23) is nonnegative, as has to be the right-hand side, proving that  $M_w \geq M_n$ .

The parameters of the molar mass distribution of some technical polymers are summarized in Table 2.2. All distributions are rather broad. Values for  $M_w/M_n$  between 1.5 and 3 are quite usual, while *PE* shows even values as high as 17. In cases, where  $U$  and  $\tilde{U}$  could be measured,  $U$  was found to be larger than  $\tilde{U}$ .



**Fig. 2.6** Molar mass distributions of the technical poly(styrene) PS N 7000 after Wolf [2]

Figure 2.6 shows the distribution functions of the molar mass of poly(styrene) PS N 7000 as determined by Wolf [2] by means of *gel permeation chromatography*. The distribution functions are linearly plotted in the upper part of the figure versus a linear scale for the molar mass, and in the lower part of the figure versus a logarithmic scale for the molar mass. Note that the distribution functions are all very asymmetric when plotted versus a linear  $M$ -scale, but nearly symmetric, when plotted versus a logarithmic  $M$ -scale. The measuring points represent the concentrations  $c_i$  of the fractions, corresponding to the molar masses  $M_i$ . From these data it is possible to calculate the number and mass densities of the molar mass, as will be explained in Sect. 3.4.

**Table 2.3** Parameters of the molar mass distribution of anionic poly(styrenes) ( $M$  in kg/mol)

Polymer	$M_n$ osm. pressure	$M_w$ light scattering	$M_w/M_n$	$M_w/M_n$ from GPC [9]	$\sqrt{U}$ , %
S1	1600	1800	1.12	—	—
S2	773	867	1.12	1.14	37
S3	392	411	1.05	1.13	36
S4	164	173	1.05	1.12	35
S5	96.2	98.2	1.02	1.10	32
S6	49	51	1.04	1.10	32
S7	19.7	19.8	1.01	1.09	30
S8	9.7	10.3	1.06	1.10	32
S9	4.6	5.0	1.09	1.10	32

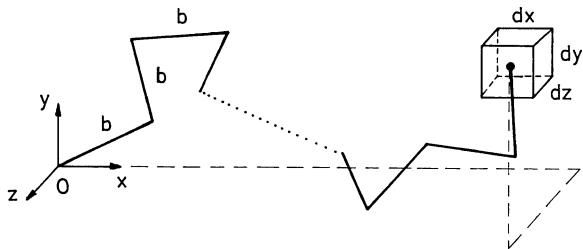
For scientific investigations it is often desirable to investigate polymers with *approximately monodisperse molar mass distributions*. These may be prepared by either *fractionation* of technical polymers or by *special control* of the *polymerization process*. The company Pressure Chemicals Co, Pittsburgh, USA, has sold *anionic poly(styrenes)* with narrow molar mass distributions, which have been often used for scientific investigations. Unfortunately, those polymers are rather expensive and, therefore, only small portions of them could be investigated. Table 2.3 shows a summary of the molecular data of some of these materials. Parameter values in the 2nd and 3rd column are taken from the producer and were determined by means of osmotic pressure and light scattering. The ratio  $M_w/M_n$  calculated from these values is very sensitive to small experimental errors and, therefore, not very reliable. A better estimate of those ratios is obtained from GPC-measurements. In the last column,  $\sqrt{U}$  is listed, which describes, according to Eq. (2.25), the variation coefficient of the number distribution density  $g(M)$ .

## 2.3 The Random Walk Problem in Three Dimensions

As to be seen from Fig. 2.2, even a short olefin chain with five carbon atoms (pentane) shows an enormous mobility, if the micro Brownian motion is fully developed. If the first carbon atom is fixed, and if full rotation around the carbon-carbon bonds can take place, the last carbon atom may occupy a very large number of spatial positions within a sphere with a radius equal to the end point distance of the completely stretched conformation. To answer the question on the shape of such a chain as a time and group average, the *random walk model* is investigated as a mathematical description of the real chain. This model is also called *random flight model* as the steps are assumed to occur in all three dimensions of the space (Fig. 2.7).

Starting from the origin of a Cartesian coordinate system,  $n$  steps of equal lengths  $b$  are performed in succession, the direction of each step being at random and independent of the directions of the previous steps. We ask for the probability

**Fig. 2.7** The random walk (flight) problem



$w(x, y, z) dx dy dz$  to arrive after the last step within a volume element with the edges  $dx, dy, dz$  around the point  $x, y, z$ . As the direction of the first step was assumed to be arbitrary, the problem has spherical symmetry and the probability function  $w(x, y, z)$  can depend only on the distance  $r$  between the *starting* and *endpoint* of the random walk.

$$w(x, y, z) = w(r) \quad \text{with} \quad r^2 = x^2 + y^2 + z^2 \quad (2.27)$$

The *completely stretched conformation* results in the *stretched length*,  $r_{\max}$ , which corresponds to the product of the number and the length of the steps of the random walk

$$r_{\max} = n \cdot b \quad (2.28)$$

As the maximum length cannot be exceeded, we have

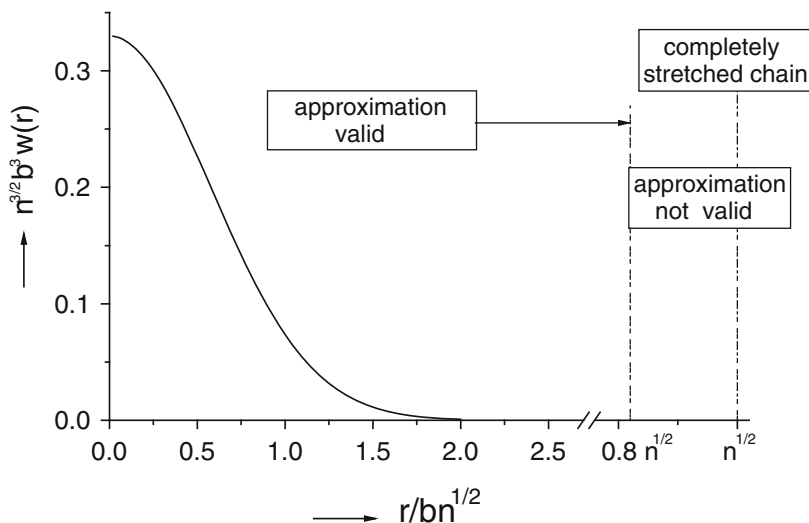
$$w(r) = 0 \quad \text{for} \quad r > r_{\max} \quad (2.29)$$

The random walk problem can be solved exactly for all values of  $n$  and  $r$ . For the derivation of the somewhat complicated solution see the excellent comprehensive presentations of Flory [10] and Yamakawa [11]. For most applications, however, it is sufficient to use a simple approximation of the exact solution, which is valid under the following conditions (Flory [10]):

- (1)  $n \gg 1$  ( $P$  is large);  $n > 10$  in practice
- (2) We only consider conformations, which are not too close to the completely stretched one  $r < r_{\max}$  in practice  $r < 0.8 r_{\max}$

Under these assumptions, the probability function of the random walk problem is given by the *Gaussian approximation*

$$w(r) \cong \left( \frac{3}{2\pi n b^2} \right)^{3/2} e^{-3r^2/2nb^2} \quad (2.30)$$



**Fig. 2.8** The Gaussian approximation for the probability density of the end point position of the random walk chain

This function shows a maximum at the position  $r = 0$  and decreases rapidly to zero with increasing  $r$ . It does not fulfill, however, the condition (2.29), showing that Eq. (2.30) cannot be valid for large values of  $r$ . The probability function,  $w(r)$ , multiplied with  $b^3 n^{3/2}$  is represented as function of  $(r/bn^{1/2})$  in Fig. 2.8. In this representation the curve does not depend any longer on the values of  $n$  or  $b$  explicitly. The function  $b^3 n^{3/2} w(r)$  shows a maximum of 0.33 at the origin, a turning point at the abscissa  $1/\sqrt{3} = 0.58$  and decreases to 22 % of its maximum value at the abscissa 1, to 0.2 % of its maximum value at the abscissa 2. In the figure, the *regions of validity* [from  $r = 0$  to  $r/(bn^{1/2}) = 0.8n^{1/2}$ ] and *invalidity* [from  $r/(bn^{1/2}) = 0.8n^{1/2}$  to  $r = \infty$ ] of the approximation, are also indicated.

For most questions in polymer physics the conditions for the validity of the Gaussian approximation will be fulfilled, as  $n$  will be of the order of magnitude of  $P$ , and as completely stretched conformations do not play a significant role in most problems. *Exceptions* to this rule are

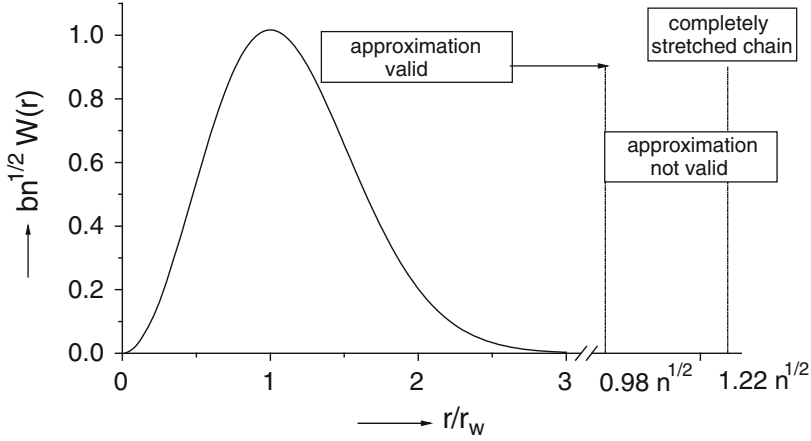
The behavior of *very stiff polymers*

The behavior of polymers with a *very low degree of polymerization*

The behavior of rubbers *at large deformations* and near rupture

The behavior of materials with *frozen stresses* at high degrees of orientation

Equation (2.30) describes the probability density of the position of the endpoint of the random walk chain in space, but not the *probability of the occurrence of chains* with a certain *end to end distance*, independent of their orientation. The latter is called the *probability density of the end to end distance*  $W(r)$ .  $W(r)dr$  is the probability to find a chain with an end to end distance between  $r$  and  $r + dr$ ,



**Fig. 2.9** Gaussian approximation for the end to end distance of the random walk chain

irrespectively of the orientation of the vector connecting its beginning and end-point. To calculate  $W(r)$ , we integrate the probability  $w(r)$  over the space bound by the spherical shells with radius  $r$  and  $r + dr$  around the origin. This is achieved by introducing spherical coordinates and leads to the result

$$W(r) = 4\pi r^2 w(r) \quad (2.31)$$

Inserting the Gaussian approximation, we find for the probability

$$W(r) = \sqrt{\frac{24}{\pi}} \cdot \frac{1}{b\sqrt{n}} \cdot \left(\frac{r}{r_w}\right)^2 e^{-(r/r_w)^2} \quad (2.32)$$

with the abbreviation

$$r_w = \sqrt{2/3} \cdot b\sqrt{n} \quad (2.33)$$

The product  $bn^{1/2} \cdot W(r)$  is shown as a function of  $r/r_w$  in Fig. 2.9.

The distribution of the end to end distance shows a maximum at the value  $r = r_w$ , meaning that  $r_w$  is the *most probable end to end distance* of the chain. The function  $W(r)$  is normalized, because

$$\int_0^\infty W(r) dr = 1 \quad (2.34)$$

as to be seen, by introducing  $\xi = r/r_w$  as a new integration variable and solving the integral by partial integration.



The most important parameter of the chain statistics is not  $r_w$  but the average of the square of the end to end distance, called the *mean square distance*:

$$\boxed{\langle r^2 \rangle \equiv \int_0^\infty r^2 W(r) dr = \frac{3}{2} r_w^2 = nb^2} \quad (2.35)$$

Equation (2.35) is obtained by the substitution of  $\xi = r/r_w$  and partial integration. The mean square distance is proportional to the number of steps in the random walk  $n$ . The quantity  $\sqrt{\langle r^2 \rangle}$ , which represents a *measure* for the *mean radius* of the polymer coil, increases proportional to the square root of the number of steps (square root of molar mass or degree of polymerization). Using (2.35), the two distribution densities of the random walk problem may be rewritten as

$$w(r) = \left( \frac{3}{2\pi \langle r^2 \rangle} \right)^{3/2} e^{-3r^2/2\langle r^2 \rangle} \quad (2.36)$$

and

$$W(r) = 3 \cdot \sqrt{\frac{6}{\pi \langle r^2 \rangle}} \cdot \frac{r^2}{\langle r^2 \rangle} \cdot e^{-3r^2/2\langle r^2 \rangle} \quad (2.37)$$

Similarly, the *averages* of all *positive integer powers* of the *end to end distance* may be calculated by repeated partial integration

$$\langle r^{2k} \rangle = \frac{1 \cdot 3 \cdot 5 \cdots (2k+1)}{3^k} \langle r^2 \rangle^k = \frac{1 \cdot 3 \cdot 5 \cdots (2k+1)}{2^k} r_w^{2k} \quad (2.38)$$

$$\langle r^{2k-1} \rangle = \sqrt{\frac{6}{\pi}} \frac{2 \cdot 4 \cdot 6 \cdots (2k)}{3^k} \langle r^2 \rangle^{(2k-1)/2} = \frac{2}{\sqrt{\pi}} \cdot \frac{2 \cdot 4 \cdot 6 \cdots (2k)}{2^k} r_w^{2k-1} \quad (2.39)$$

These formulae are valid for all positive integer values of  $k$  and for  $k = 0$ .

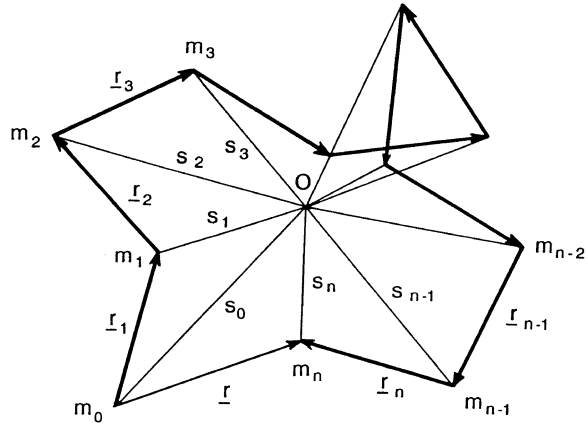
Equation (2.35) may be derived in another, more illustrative way, which has been used frequently by Flory [10]. Let  $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n$  be the connecting vectors representing the  $n$  steps of the random walk (cf. Fig. 2.10). Each of those vectors has the same length  $b$ , but an arbitrary direction in space.

The *end to end vector* of the random walk is the *sum* of all the *connecting vectors*

$$\underline{r} = \underline{r}_1 + \underline{r}_2 + \underline{r}_3 + \cdots + \underline{r}_n \quad (2.40)$$

Its absolute value,  $r$ , which equals the end to end distance, is found as the square root of the scalar product of the vector  $\underline{r}$  with itself:

**Fig. 2.10** Definition of the end to end distance as the sum of the connecting vectors and the definition of the radius of gyration of the random walk (flight) chain



$$\underline{r} \cdot \underline{r} = \sum_{i=1, k=1}^n (\underline{r}_i \cdot \underline{r}_k) \quad (2.41)$$

The double sum over  $i$  and  $k$  may be separated into a sum with equal indices and a sum with different indices:

$$r^2 = \sum_{i=1, k=1}^n (\underline{r}_i \cdot \underline{r}_k) = \sum_{i=1}^n (\underline{r}_i \cdot \underline{r}_i) + \sum_{\substack{i=1, k=1 \\ i \neq k}}^n (\underline{r}_i \cdot \underline{r}_k) = nb^2 + \sum_{\substack{i=1, k=1 \\ i \neq k}}^n (\underline{r}_i \cdot \underline{r}_k) \quad (2.42)$$

This equation is valid for each chain of  $n$  steps of equal length, independently of the law specifying the direction of the successive steps.

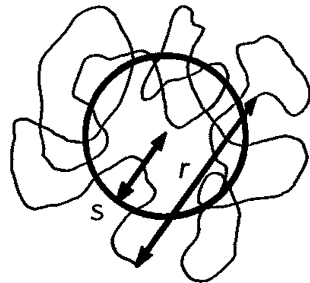
The average of the second sum will vanish for the random walk chain, as the angle between two different connecting vectors is arbitrary and the angle  $\pi - \vartheta$  occurs with equal probability as the angle  $\vartheta$ . In the first case, the scalar product of the two vectors will contribute with  $-b^2 \cos \vartheta$  to the sum, in the second case with  $b^2 \cos \vartheta$ , and, on the average, both terms will cancel each other, i.e.,

$$\langle (\underline{r}_i \cdot \underline{r}_k) \rangle = 0 \quad \text{for } i \neq k \quad (2.43)$$

Inserting this into Eq. (2.42), leads again to Eq. (2.35) for the random walk chain. Though both equations are identical, their requirements are different. We used the Gaussian approximation for deriving (2.35), but the weaker restriction of random walk only, now.

Besides the end to end distance, a further measure is often introduced to characterize the coil dimensions of a polymer, the so called *radius of gyration*  $s$ . This is explained referring to Fig. 2.10. The random walk chain of  $n$  steps contains  $n + 1$  points (the starting and end points of the vectors), indicated by  $m_0, m_1, m_2$

**Fig. 2.11** End to end distance  $r$  and radius of gyration  $s$  of the random walk chain



...  $m_n$ . Assuming that the mass of the chain is uniformly distributed over these  $(n + 1)$  segments, the center of gravity 0 of the segments may be calculated as well as the distances  $s_i$  ( $i = 0$  to  $n$ ) of the segments from it. The mean value of the squares of the distances yields the *square* of the *radius of gyration*

$$s^2 = \frac{1}{n + 1} \sum_{i=0}^n s_i^2 \quad (2.44)$$

For the random walk chain, it is possible to calculate the expectation value of the square of the radius of gyration (for a derivation see e.g., [10, 11]):

$$\langle s^2 \rangle = \frac{1}{6} \langle r^2 \rangle \quad (2.45)$$

The radius of gyration may be considered as a *measure* for the *dimension* of the *coil*. From Eq. (2.45), it is seen, however, that the radius of gyration is smaller than half of the end to end distance. The reason for that is the fact that in the random walk chain the concentration of segments is much higher in the center of the coil, than in its outer regions. This is indicated in Fig. 2.11.

## 2.4 Macromolecules in Solution

Molar masses are determined in dilute solution. Therefore, solubility is an essential requirement for the determination of molar masses of polymers. The methods most frequently used are presented in Table 2.4:

In order to understand why the determination of molar masses is to be performed in dilute solution, we consider the shape of the polymer in solution. Micro-Brownian motion is excited in solution, therefore macromolecules which are not extremely stiff will assume the shape of coils with the radius  $h$  depending on

molar mass  
interaction with the solvent  
internal mobility of the macromolecule

**Table 2.4** Methods of determination of molar masses and their range of applicability

Method	Average obtained	Range of applicability, kg/mol
Osmotic pressure	$M_n$	5–1000
Viscometry	$M_v$	0.1–1000
Light scattering	$M_w$	0.1–1000
Ultracentrifuge	$M_z$	10–2000
Gel permeation chromatography	$c(M)$	0.1–1000

A large number of solvent molecules, however, is included within one macromolecular coil. Therefore  $d_m$ , *the average density of the macromolecule in the coil*

$$d_m = \frac{\text{mass of the macromolecule}}{\text{volume of the coil}} \quad (2.46)$$

will be small. The properties of the isolated coils can be determined in dilute solution only, as the coils should not penetrate, not even touch, each other. Therefore, *the weight concentration of the polymer in the solution*

$$c = \frac{\text{mass of the polymer}}{\text{volume of the solution}} \quad (2.47)$$

should be chosen adequately small, viz.,  $c \approx 1\text{--}50$  g/l. On the other side, the dilution should not be too extreme, as the properties of the solution should significantly differ from those of the pure solvent to be able to measure their difference. This requirement often constitutes an experimental difficulty.

For a better understanding of the properties of a polymer solution, some basic concepts of its thermodynamic properties are to be discussed, especially the question of the characterization of the quality of the solvent. We consider solution or mixing at constant temperature  $T$  and constant pressure  $p$ , i.e., an isothermal-isobaric dissolving process. The thermodynamic potential under these circumstances is the *free enthalpy*

$$G = U + pV - TS \quad (2.48)$$

where  $U$  designates the internal energy,  $p$  the pressure,  $V$  the volume,  $T$  the absolute temperature and  $S$  the entropy. Under isothermal-isobaric conditions, a system tends to achieve a state with minimum free enthalpy.

We solve  $n_2$  mol of the polymer into  $n_1$  mol of the solvent and designate

$(G)_1$  the free enthalpy of the solvent before the process of solution

$(G)_2$  the free enthalpy of the polymer before the process of solution

$(G)_L$  the free enthalpy of the system after the process of solution

The *free enthalpy of mixing*  $G_m$  is the difference of the enthalpies after and before the dissolving process and may be decomposed into its energetic part  $U_m$ , its entropic part  $TS_m$  and its volumetric part  $pV_m$

**Table 2.5** Quality of the solvent and heat balance of the solution process

	Quality of the solvent	Heat balance of the dissolving process
$U_m < 0$	Very good	Exothermal
$U_m = 0$	Good	Athermal
$U_m > 0$	Moderate to poor	Endothermal

$$G_m \equiv (G)_L - (G)_1 - (G)_2 = U_m + pV_m - TS_m \quad (2.49)$$

$S_m$  is the always positive *mixing entropy*,  $V_m$  the change in volume during the mixing process (which may be neglected for condensed phases) and  $U_m$  the *mixing energy*, which may be positive or negative. The dissolving process is classified according to the sign of  $U_m$  (Table 2.5).

For the characterization of the properties of the solution we need an *intensive* quantity (which depends on  $T$ ,  $p$ , and the composition of the solution, but not on its mass). We describe the composition of the solution by the ratio of the *mole numbers*

$$z = n_2/n_1 \quad (2.50)$$

or by their *mole fractions*

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{1}{1 + z} \quad (2.51)$$

and

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{z}{1 + z} \quad (2.52)$$

It is shown in thermodynamics that every *extensive* quantity may be written as sum of the corresponding *intensive* quantities multiplied with their mole numbers

$$G_m(T, p, n_1, n_2) = n_1\mu_1(T, p, z) + n_2\mu_2(T, p, z) \quad (2.53)$$

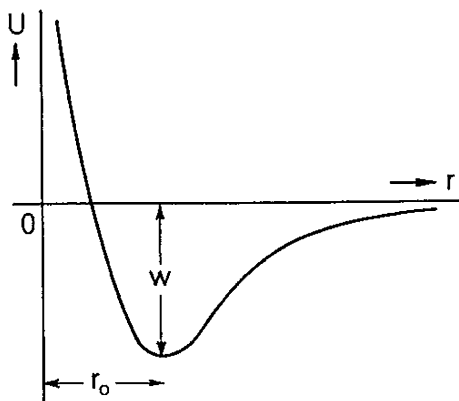
$\mu_1$  and  $\mu_2$  are *intensive quantities* and may be calculated by partial differentiation of the extensive quantity  $G_m$  with respect to their respective mole numbers:

$$\mu_1(T, p, z) = \left( \frac{\partial G_m}{\partial n_1} \right)_{n_2, T, p} \quad (2.54)$$

and

$$\mu_2(T, p, z) = \left( \frac{\partial G_m}{\partial n_2} \right)_{n_1, T, p} \quad (2.55)$$

**Fig. 2.12** Potential energy of two (parts) of molecules versus their distance



$\mu_1$  is called the *chemical potential of the solvent* (or the *free enthalpy of dilution*),  $\mu_2$  the *chemical potential of the solute* (or the *free enthalpy of solution*). A further intensive quantity may be used for the characterization of the solution, called the *average molar free enthalpy of mixing* and is defined by the equation:

$$\overline{G}_m(T, p, z) \equiv \frac{G_m(T, p, n_1, n_2)}{n_1 + n_2} = x_1 \mu_1(T, p, z) + x_2 \mu_2(T, p, z) \quad (2.56)$$

We turn to the molecular interpretation of the mixing energy. The energy of interaction of two solvent molecules or parts of two macromolecules as a function of their distance  $r$  is sketched in Fig. 2.12.

At the distance  $r_0$  both molecular parts are in equilibrium, at smaller distance ( $r < r_0$ ) *strong repelling forces* occur due to the interaction of the electron shells, at larger distance *weak attractive forces* occur. The depth of the energy minimum  $w$  at  $r = r_0$  depends on the chemical composition of both partners involved (note that  $w$  is always negative!).

Solvent molecule—solvent molecule	$w_{11}$
Structural unit of the polymer—structural unit of the polymer	$w_{22}$
Structural unit of the polymer—solvent molecule	$w_{12}$

During the process of dissolving the contact of two solvent molecules is broken up, as well as the contact of two parts of macromolecules, and two new contacts of parts of the macromolecule and a solvent molecule are created. The change in energy due to this process will be

$$w = 2w_{12} - w_{11} - w_{22} \quad (2.57)$$

As the sign of  $U_m$  is the same as that of  $w$ , three cases can be regarded:

1.  $w < 0$  and  $U_m < 0$  : *very good solvent*; The process of dissolving is driven energetically, too, and is exothermal; the macromolecule is soluble at all temperatures, the solvent molecules are driven into the coil, which is inflated, i.e., its radius  $h$  becomes large.

2.  $w = 0$  and  $U_m = 0$ : *athermal solvent*; the process of dissolving is driven by entropy changes, only; the macromolecule is soluble at all temperatures, the coil is inflated.
3.  $w > 0$  and  $U_m > 0$ : *poor solvent*; the process of dissolving is a competition between the entropy effect, driving the molecule into solution, and the energy effect, driving the molecule to precipitate. The process of dissolving is endothermal, the solubility of the polymer will increase with increasing temperature. The solvent molecules are squeezed out of the coil, the radius of the coil  $h$  will become small.

Flory [12] and Huggins [13] have proposed the following simple expression as an approximation for the free enthalpy of mixing

$$G_m = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2) \quad (2.58)$$

Here,  $v_1$  and  $v_2$  are the *volume concentrations* of *solvent* and *polymer*,

$$v_1 = \frac{V_1 n_1}{V_1 n_1 + V_2 n_2} \quad (2.59)$$

and

$$v_2 = \frac{V_2 n_2}{V_1 n_1 + V_2 n_2} \quad (2.60)$$

with  $V_1$  and  $V_2$  being their molar volumes.  $R$  is the *gas constant* and  $k$  the *Boltzmann* constant

$$R = k \cdot N_A = 8.3143 \text{ J/K mol} \quad (2.61)$$

$$k = 1.3805 \cdot 10^{-23} \text{ J/K} \quad (2.62)$$

$\chi$  is the “*Flory-Huggins parameter*”, which characterizes the interaction between polymer and solvent. It consists of a contribution,  $\chi_0$ , to the mixing entropy and a contribution, which is proportional to the mixing energy  $w$

$$\chi = \chi_0 + \beta \frac{w}{kT} \quad (2.63)$$

$\chi_0$  is positive and  $\beta$  is a coordination number of the order of unity. If Eq. (2.58) is applied to the description of the free enthalpy of polymer solutions,  $\chi$  is experimentally found not to be constant but to be slightly depending on  $T$ ,  $M$ , and the concentration  $v_2$ . Using (2.54), (2.58), (2.59), and (2.60), we find after some elementary calculations, the following expression for the free enthalpy of dilution

$$\mu_1 = RT \left( \ln v_1 + \left( 1 - \frac{V_1}{V_2} \right) v_2 + \chi_1 v_2^2 \right) \quad (2.64)$$

**Table 2.6** Solvents, precipitants, and Theta-solutions of some polymers

Polymer	Solvent (T, °C) <sup>a</sup>	Theta-solution (T, °C)	Precipitants
PE-HD	Hydrocarbon (>80) Hydrogenated Hydrocarbon (>80)	n-hexane (133)	All organic solvents At room temperature
PE-LD	Hydrocarbon (>60) Hydrogenated Hydrocarbon (>60)	Same as for PE-HD	Same as for PE-HD
PP atactic	Hydrocarbon Hydrogenated Hydrocarbon	i-amylacetate (34) Cyclohexanone (92)	Polar organic solvents
PA 6.6	Phenols Formic acid	2.3 mol KCl in 90 % Formic acid (25)	Hydrocarbons Chloroform
PIB	Hydrocarbons Tetrahydrofuran (THF)	Benzene (22.8)	Butanol Methanol
PMMA	Benzene Xylene Chloroform	Butanon/isopropanol 50/50 (23) m-xylene (24)	Hexene Cyclohexane Methanol
PS	Chloroform Benzene	Cyclohexane (34)	Saturated hydrocarbons alcohols
PVC	THF Cyclohexanone	THF/H <sub>2</sub> O 89/11 (30)	Hydrocarbons Alcohols
PC	Benzene Chloroform	Chloroform/ethanol 74.5/25.5 (18)	Aliphatic hydrocarbons Acetone

<sup>a</sup> No indication of a temperature: soluble at room temperature

$\chi_1$  is a new *Flory-Huggins parameter*, related to  $\chi$  by the equation

$$\chi_1 = \chi + \frac{n_1}{v_2} \left( \frac{\partial \chi}{\partial n_1} \right)_{n_2, T, p} = \chi - v_1 \left( \frac{\partial \chi}{\partial v_2} \right)_{T, p} \quad (2.65)$$

If  $\chi$  is independent of  $v_2$ , we have simply  $\chi_1 = \chi$ . As in poor solvents the solubility increases with temperature, a temperature will be found, at which the influence of the occupied volume of the polymer molecules is just compensated by the influence of the polymer-solvent interaction. This temperature is called the “*Theta-temperature*” and plays an important role in polymer physics. At the  $\Theta$ -temperature the shape of polymer molecules may be calculated by statistics without taking into account the influence of the occupied volume or the polymer-solvent interaction. This solution is called a  $\Theta$ -*solution*. The concept of the occupied volume and the  $\Theta$ -temperature will be explained in more detail in the Sect. 3.1.



For a very large number of polymers, extensive tables have been given of solvents and precipitants by Bloch [14] and of  $\Theta$ -solutions by Elias [15]. A few examples of solvents, precipitants and  $\Theta$ -solutions for some polymers are given in Table 2.6.

Experimental methods to determine thermodynamic properties of polymer solutions and  $\Theta$ -temperatures will be described in the next chapter. The reader can find extensive tables for the Flory-Huggins parameters for many polymers, solvents and temperatures in [16].

## 2.5 Statistical Shape of Linear Macromolecules in $\Theta$ -Solution

The linear macromolecule in theta-solution may not be directly identified with the random walk chain. Though the influence of the excluded volume and the interaction with the solvent molecules may be neglected in a theta-solution, the detailed molecular structure of the molecule in question determines the degrees of freedom for the internal motions and has to be considered in each case separately. The presence of fixed valence bonds and the partially hindered rotation around these bonds enlarge the coil dimensions. Nevertheless, it is possible in many cases to calculate the mean square end to end distance. Most of these calculations have been performed and presented by Flory [10].

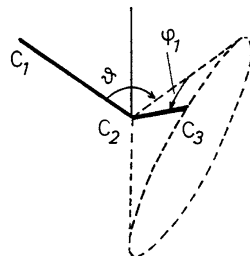
The simplest case is the *valence bond chain with free rotation*. Consider a linear not branched chain of a vinyl polymer, for which all bonds of the main chain are single carbon-carbon bonds. The molecule consists of  $n_0 + 1$  carbon atoms, connected by  $n_0$  bond vectors  $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_{n_0}$ . Let the length of each bond vector be  $b_0$ , its bond angle  $\vartheta$ . Apart from movements of side groups, the shape of the main chain (its *conformation*) is fixed, if the  $n_0 - 1$  rotational angles around the main bonds,  $\varphi_1, \varphi_2, \dots, \varphi_{n_0-1}$  are fixed. The definition of such an angle is illustrated in Fig. 2.13 for the first two bond vectors and for the first rotational angle  $\varphi_1$ .

The zero points of the rotational angles are chosen in such a way, that the set  $\varphi_1 = \varphi_2 = \dots \varphi_{n_0-1} = 0$  corresponds to the completely stretched conformation. The fixed angle between successive valence bonds has an effect on the value of  $\langle r^2 \rangle$ . Equation (2.42) remains valid, but the average values of the second term on the right-hand side of this equation do not longer vanish. The averages of the scalar products of two different bond vectors may be evaluated as shown by Flory [10] in a very elegant manner. For the scalar product of two successive bond vectors one finds

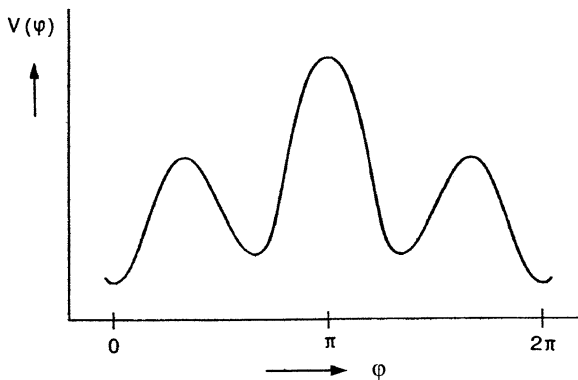
$$(\underline{r}_1 \cdot \underline{r}_2) = b_0^2 \cos(\pi - \vartheta) = -b_0^2 \cos \vartheta \quad (2.66)$$

The scalar product  $(\underline{r}_1 \cdot \underline{r}_3)$  depends on the value of the second rotational angle  $\varphi_2$

**Fig. 2.13** The definition of the rotational angle  $\varphi_1$



**Fig. 2.14** Potential energy as a function of the rotational angle



$$(\underline{r}_1 \cdot \underline{r}_3) = b_0^2 (\cos^2 \vartheta + \sin^2 \vartheta \cos \varphi_2) \quad (2.67)$$

As all values of  $\varphi_2$  are equally probable (free rotation), we have to integrate over all values of  $\varphi_2$  and to divide by  $2\pi$  in forming the average  $\langle (\underline{r}_1 \cdot \underline{r}_3) \rangle$ . In similar way all terms of the double sum of Eq. (2.42) may be calculated with the result

$$\langle r^2 \rangle_{\vartheta} = n_0 b_0^2 \cdot \frac{1 - \cos \vartheta}{1 + \cos \vartheta} \quad (2.68)$$

For vinyl polymers  $\cos \vartheta = -1/3$  and the quotient in Eq. (2.68) becomes 2.

*The valence bond chain with hindered rotation.*

If the rotation around valence bonds is hindered by the presence of side groups, the angles  $\varphi_1, \varphi_2, \dots, \varphi_{n_0-1}$  are no longer equally probable.

If only side groups of neighbored C-atoms hinder each other, the hindering effect may be described by the potential energy of a part of the chain as a function of the rotational angle  $V = V(\varphi)$  as shown in Fig. 2.14.

To calculate the expectation value of the scalar products at the right-hand side of Eq. (2.42), each term has to be weighed with the probability of occurrence of the corresponding rotational angle. Instead of (2.68), one obtains [10]

$$\langle r^2 \rangle_{\Theta} = n_0 b_0^2 \cdot \frac{1 - \cos \vartheta}{1 + \cos \vartheta} \cdot \frac{1 - \langle \cos \varphi \rangle}{1 + \langle \cos \varphi \rangle} \quad (2.69)$$

The expectation value  $\langle \cos \varphi \rangle$  has to be calculated using the Boltzmann factor (notice the symmetry of  $V$  with respect to  $\varphi = \pi$  !):

$$\langle \cos \varphi \rangle = \frac{\int_0^{\pi} \cos \varphi e^{-V(\varphi)/kT} d\varphi}{\int_0^{\pi} e^{-V(\varphi)/kT} d\varphi} \quad (2.70)$$

#### *More complicated macromolecules*

If the macromolecule is more complicated, e.g., if short parts of the main chain are not movable, or if the interactions extend further than between neighbored side groups, a calculation of the end to end distance is still possible. As long as the interactions occur only between side groups of carbon atoms which are not too far apart from each other in the completely stretched conformation, a result of the following form is obtained [10]

$$\langle r^2 \rangle_{\Theta} = n_0 \cdot b_0^2 \cdot C \quad (2.71)$$

where  $b_0$  is the distance of the singular C–C bond,  $n_0$  the number of bonds in the principal chain and  $C$  is a constant depending on the detailed structure of the molecule. In many cases, it is possible to calculate  $C$  [16]; in very complicated cases,  $C$  may be determined experimentally by osmotic pressure or light scattering measurements (Compare Table 3.2 for examples of the values of  $C$ ).

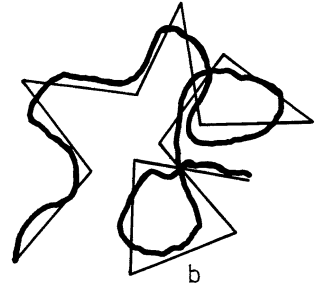
#### *The statistical equivalent random walk chain*

So far, we have considered the values of the average of the mean square distance  $\langle r^2 \rangle_{\Theta}$ , only. If this quantity may be described by Eq. (2.71), being proportional to the number of bonds,  $n_0$ , the probability of the end point position will be *Gaussian*. Inserting the values found in Eqs. (2.6), (2.68) or (2.69) into (2.36) and (2.37) the *probability densities* of the *end point position* and the *end to end distance* remains valid for linear macromolecules in  $\Theta$ -solution.

To each linear macromolecule in theta-solution a *statistical equivalent random walk chain* with  $n$  steps of length  $b$  may be attributed, which behaves equal with regard to their distribution in space. Their completely stretched lengths and their mean square distances, as well correspond to each other.

The *length* and *number of steps* of the *statistical equivalent random walk chain* may be defined by the equations:

**Fig. 2.15** The macromolecule and its statistical equivalent random walk chain



$$n \cdot b^2 = \langle r^2 \rangle_{\theta} = n_0 \cdot b_0^2 \cdot C \quad (2.72)$$

and

$$n \cdot b = r_{\max} \quad (2.73)$$

Or vice versa:

$$b = \langle r^2 \rangle_{\theta} / r_{\max} = n_0 b_0^2 C / r_{\max} \quad (2.74)$$

and

$$n = (r_{\max})^2 / \langle r^2 \rangle_{\theta} \quad (2.75)$$

$b$  is called *Kuhn's statistical segment length*;  $r_{\max}$  is the completely stretched length of the molecule, which may be calculated from its structural formula. The manner, in which the statistical equivalent random walk chain may follow the shape of the real chain, has been indicated in Fig. 2.15.

For the special case of a *vinyl polymer* we have two C–C bonds in one structural unit, the bond length  $b_0 = 0.154$  nm, and the bond angle  $\vartheta = 109.47^\circ$  ( $\cos \vartheta = -1/3$ ) and therefore

$$r_{\max} = b_0 n_0 \cos((\pi - \vartheta)/2) = \sqrt{\frac{2}{3}} b_0 n_0 = \sqrt{\frac{2}{3}} 2b_0 \cdot P = \sqrt{\frac{8}{3}} b_0 \cdot \frac{M}{M_g} \quad (2.76)$$

with  $\sqrt{8/3} b_0 = 0.251$  nm. Inserting Eq. (2.76) into Eqs. (2.74), (2.72), and (2.45), yields the following expressions for *Kuhn's statistical segment*, the *mean square end to end distance* and the *mean square radius of gyration* in *theta solution*:

$$b = \sqrt{\frac{3}{2}} C \cdot b_0 \quad (2.77)$$

$$\boxed{\langle r^2 \rangle_{\Theta} = \alpha_{\Theta}^2 \cdot P} \quad (2.78)$$

$$\boxed{\langle s^2 \rangle_{\Theta} = \beta_{\Theta}^2 \cdot P} \quad (2.79)$$

with

$$\alpha_{\Theta} = b_0 \cdot \sqrt{2 \cdot C} \quad (2.80)$$

and

$$\beta_{\Theta} = \alpha_{\Theta} / \sqrt{6} = b_0 \cdot \sqrt{C/3} \quad (2.81)$$

Some values for  $C$ ,  $b/b_0$ , and  $\beta_{\Theta}/b_0$  will be given in Table 3.3.

## 2.6 Statistical Shape of Macromolecules in Good Solvents

In good solvents the interaction between macromolecules and solvent molecules has to be considered. This interaction influences the shape of the macromolecule and the statistical distribution of its segments. The mathematical problem becomes much more complicated and is still unsolved (cf. [10]). However, it should be mentioned, that the coils will be widened in good solvents, i.e.,

$$\langle r^2 \rangle > \langle r^2 \rangle_{\Theta} \quad \text{and} \quad \langle s^2 \rangle > \langle s^2 \rangle_{\Theta}$$

Neither Eq. (2.45) nor Eq. (2.71) remain valid in this case. Instead, the *mean square values* of the *end to end distance* and of the *radius of gyration* increase more than proportional to the degree of polymerization  $P$ :

$$\langle r^2 \rangle = \alpha^2 \cdot P^{1+\varepsilon} \quad (2.82)$$

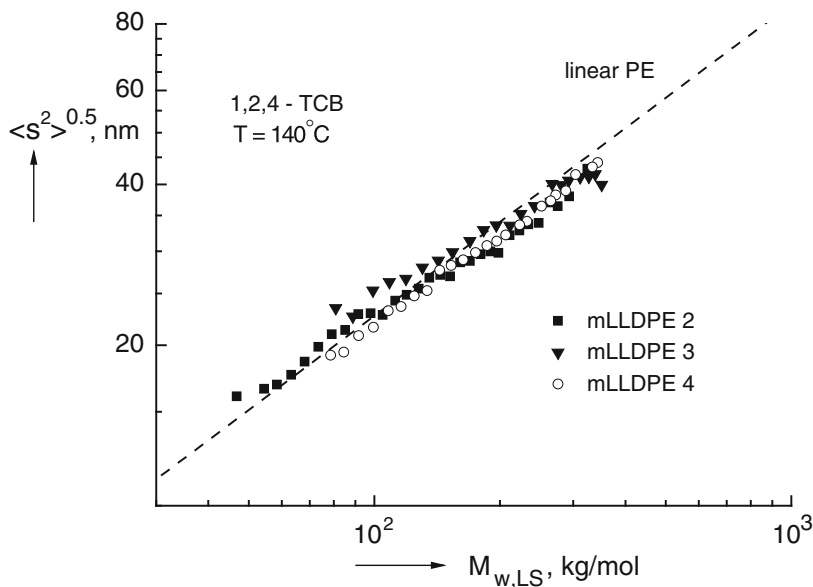
and

$$\langle s^2 \rangle = \beta^2 \cdot P^{1+\rho} \quad (2.83)$$

with  $\varepsilon$  and  $\rho$  being positive numbers. Though power laws of the form of Eqs. (2.82) and (2.83) have not been derived theoretically up to now, their validity can be checked experimentally. Using gel permeation chromatography (GPC) coupled with multi-angle laser light scattering (MALLS) it is possible to investigate

**Table 2.7** Parameter values of the relation (2.83) between the mean square radius of gyration and the degree of polymerization for the linear vinyl polymers poly(propylene) and poly(ethylene) in the good solvent trichlorobenzene (TCB)

Polymer, solvent, T °C			$\beta$ , $10^{-10}$ m	$\rho$	Range for P, kg/mol	Lit.
PP	TCB	140	1.52	0.17	$2.5 \cdot 10^3 < P < 10^5$	[8, 17]
PE	TCB	140	1.66	0.16	$10^3 < P < 2 \cdot 10^4$	[8, 17]

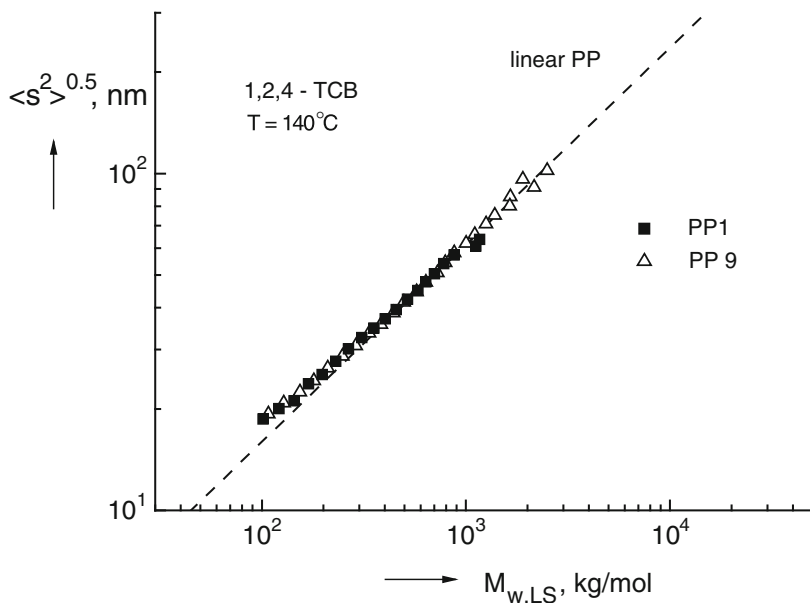


**Fig. 2.16** Square root of the mean square radius of gyration versus the absolute weight average molar mass  $M_{w,LS}$  determined by GPC-MALLS for three linear PE. The dashed line represents the square root of Eq. (2.83) with the parameter values given in Table 2.7. Reproduced from [7]

the relation between  $\langle s^2 \rangle$  and  $M_w$  for polymer solutions in good solvents. For some linear vinyl polymers, power laws of the form of Eq. (2.83) have been found to be valid, as summarized in Table 2.7.

Two examples of measurements of this kind, taken from [8] are given in Figs. 2.16 and 2.17.

Figure 2.16 shows the square root of the mean square radius of gyration versus the weight average molar mass measured by light scattering for GPC-fractions of three linear low density PE in trichlorobenzene (TCB) at 140 °C, [8]. The broken line represents the square root of Eq. (2.83) with the parameter values given in Table 2.7. The three polymers, designated as mLLDPE 2–4 are metallocene linear low density poly(ethylenes), which are assumed to contain no long chain branches. They have similar molar mass distributions and similar values of  $M_w$ , but slightly different comonomer composition. Their values of  $\langle s^2 \rangle^{1/2}$  lie on or closely to the



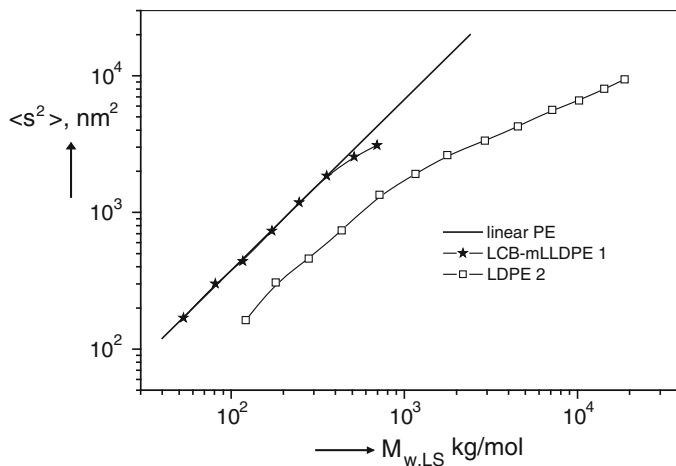
**Fig. 2.17** Square root of the mean square radius of gyration versus the absolute weight average molar mass  $M_{w,LS}$  determined by GPC-MALLS for two linear *PP*. The *dashed line* represents the square root of Eq. (2.83) with the parameter values given in Table 2.7. Reproduced from [7]

(dashed) reference line for *linear PE*. This result confirms, that not branched polymers show a power law relation between  $\langle s^2 \rangle^{1/2}$  and  $M_w$ . It is well known that this is no longer true, if the polymer contains long chain branches. Moreover,  $\langle s^2 \rangle^{1/2}$  is then found to be smaller than the radius of gyration of a linear molecule with the same  $M_w$  (c.f. Sect. 2.7).

Figure 2.17 shows the square root of the mean radius of gyration versus the weight average of the molar mass  $M_w$  for two linear *PP* in TBC at 140 °C, designated as *PP 1* and *PP 9* [8]. The dashed line represents the square root of Eq. (2.83) with the parameter values given in Table 2.7. The polymers are assumed to be linear with similar molar mass distributions but different weight average of the molar mass measured by light scattering. Again, the values of  $\langle s^2 \rangle^{1/2}$  lie closely to the (dashed) reference line for *linear PP*, which differs slightly from the reference line for *linear PE*.

## 2.7 Analysis of Branched Macromolecules

As any branching within a polyolefin chain means a change of the mobility of the carbon atom it is attached to, the melt-state  $C^{13}$  *nuclear magnetic resonance*, in principle, is a suitable method to detect branches. Its elegance lies in the fact that a



**Fig. 2.18** Mean square radius of gyration  $\langle s^2 \rangle$  as a function of the absolute weight average molar mass  $M_{w,LS}$  measured by light scattering for polyethylenes of various branching structures [7]

quantitative picture of the branching sites can be obtained without any model assumptions. But according to [18] the analytical power of this technique is restricted insofar as it is able to merely discriminate between attached molecules up to 6 carbon atoms. Longer molecules which are typical of long-chain branches do not give particular signals. This physical fact has two consequences. A reliable information on short-chain branching can be obtained, only, if any long-chain branches are absent and, the other way round, conclusions with respect to long-chain branching can be drawn from NMR-measurements under the precondition that no short-chain branches longer than 6 C-atoms are present. Particularly the last requirement is very difficult to fulfill in the case of technically produced materials. It is well established, for example, that low density polyethylenes may contain a respectable number of short-chain besides long-chain branches.

Similar arguments hold for results from infrared-spectroscopy which is easy to perform. In the case of polyethylenes the number of  $\text{CH}_3$ -groups obtained by this method can belong to short-chain or long-chain branches as well.

Therefore, the gel-permeation chromatography coupled with multi-angle laser-light scattering (*GPC-MALLS*) as sketched in Sect. 3.4 is a very valuable method to get an insight into the long-chain branching structure of a polymer. This potential is demonstrated by Fig. 2.18 which displays in a double-logarithmic plot the mean squared radius of gyration of a low density polyethylene (LDPE) which is well known for its long-chain branching as a function of the absolute value of the weight average molar mass determined by light scattering in comparison to the corresponding curve for a linear polyethylene. It is obvious that the coil



dimensions of the LDPE are significantly smaller than those of the linear counterpart. This finding can be explained by the assumption that the branches are able to at least partly fill the free space between the segments of the backbone of the molecules. According to Fig. 2.18 the differences of the coil dimensions between linear and long-chain branched molecules become the more pronounced the higher the molar mass indicating an increasing effect of branching.

A distinctly different result is found from Fig. 2.18 for the long-chain branched metallocene-catalyzed linear low density polyethylene (LCB-mLLDPE 1). Only at higher molar masses a deviation from the straight line of the linear material occurs. This finding can be interpreted in a way that the existence of long-chain branches is restricted to the longer molecules and the shorter ones behave linear although they contain short-chain branches according to their chemical structure. As a side effect this result demonstrates that the influence of comonomers on the coil dimension cannot be detected by *GPC-MALLS* at least for the compositions commonly found with LLDPE.

For a more quantitative discussion of the differences in coil size between linear and branched molecules the so-called *branching index*

$$g = \frac{\langle s^2 \rangle_{\text{br}}}{\langle s^2 \rangle_{\text{lin}}} \quad (2.84)$$

is defined. The index “br” denotes the mean square radius of gyration of the branched, the index “lin” that of the linear species taken at the same molar mass.

Although clearly defined and very descriptive there have been only very few theories up to now which try to correlate the branching index with the branching structure [19, 20]. For example, for monodisperse star polymers the conformation of which can be described by the theory of undisturbed chain statistics the relationship

$$g = (3f - 2)/f^2 \quad (2.85)$$

between  $g$  and the functionality  $f$  of a branching point is given by Zimm and Stockmayer in [19].

Furthermore, in [19] the following relationship between  $g$  and the number of statistically distributed trifunctional branching centers  $m$  per molecule is derived for monodisperse polymers:

$$g \approx \left[ (1 + m/7)^{0.5} + 4m/9\pi \right]^{-0.5} \quad (2.86)$$

From  $m$ , the number of branching points per monomer unit  $M_g$  can be assessed as

$$\lambda = mM_g/M \quad (2.87)$$

with  $M$  being the molar mass. Under the assumption of equal lengths of the segments between the branching points their molar mass  $M_s$  follows as

$$M_s = M/(2m + 1) \quad (2.88)$$

The prerequisite of monodispersity for the application of the Zimm-Stockmayer theory is fulfilled for an evaluation of the *GPC-MALLS* measurements as the fractions obtained are very narrowly distributed. The requirement of trifunctionality is very difficult to assess, however, as the branching structure depends on the polymerization conditions. Therefore, Eqs. (2.85) to (2.88) are of a very limited value for the description of real long-chain branched polymers, but in some cases they may be helpful for a qualitative comparison of various products.

## 2.8 Size of Macromolecules in the Glassy and Molten State

The large importance of the  $\Theta$ -solution is due to the fact that shape and extension of linear macromolecules may be experimentally determined and calculated by means of Gaussian statistics. Moreover, the coil dimensions of linear macromolecules in the glassy state and in the melt are similar to those in  $\Theta$ -solution. This has been assumed since long [10], but the experimental proof was conducted by Fischer and Dettenmaier in 1978 [21]. Their experiment is based on the strong difference in neutron-scattering between molecules containing hydrogen or deuterium atoms. If for a small part of the molecules present in the solid polymer hydrogen atoms are replaced by deuterium, it is possible to detect these molecules by small-angle neutron scattering similar to the characterization of ordinary macromolecules in dilute solution by means of light scattering. In both cases the radius of gyration of the coil is obtained.

For linear vinyl polymers in  $\Theta$ -solution the relation (2.89) between the radius of gyration and the degree of polymerization

$$\langle s^2 \rangle = \beta_\Theta^2 \cdot P \quad (2.89)$$

holds with  $\beta_\Theta$  being a constant only weakly depending on temperature. This relation remains valid with the same value of the constant  $\beta$  for macromolecular coils in the solid and molten state as proven by Fischer and Dettenmaier [21]. The values from their publication are given in Table 2.8. The coefficients  $\beta$  as determined by light scattering or viscometry in  $\Theta$ -solution are compared with results of

**Table 2.8**  $\beta = \sqrt{\langle s^2 \rangle / P}$  for polymers in the solid and molten state and in  $\Theta$ -solution

Polymer	Range of molar mass in kg/mol	$\beta$ in $10^{-10}$ m solid or molten	$\beta$ in $10^{-10}$ m in $\Theta$ -solution
PMMA	6–1000	2.56	2.20
PS	20–1000	2.81	2.76
SI	200	2.28	2.24
PVC	70–200	3.24	2.93
PE	10–80	2.33	2.28
	60–400	2.44	2.28

neutron scattering in the solid and molten state of various polymers in a wide range of molar masses. The agreement of the results in  $\Theta$ -solution and in the bulk is very good.

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