

E 2 Polymers: Structure

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Contents

1	Introduction	2
2	Polymer Chain Models and Architecture	3
3	Scattering: intra- and inter-chain contributions.....	7
4	Blend of linear Polymers	9
5	Tri-block copolymers	13
6	Branched Chains	15
7	Summary	18
	Appendix	19
	References	20

1 Introduction

A topical application of this spring school which deals with every day life is polymers. Polymers have a very rich behaviour and are ideal for investigations by means of neutron scattering techniques. As reported in the appropriate scattering introduction, this is due to the natural difference between a proton and a deuteron. Although chemically virtually no other properties are induced if some H's are replaced by some D's, this labelling allows to study e.g. the effect of different environments on the structure of polymers, on parts of the chains and so on. This is a strong advantage over scattering by xrays which is limited to systems which differ considerably in electron density. The H/D labelling does not change the xray scattering patterns. Nevertheless, the latter probe is very often used as a valuable complementary technique, especially in multiphase systems.

The following small treatise on polymers focuses only on the determination of their structure using the technique of Small Angle Neutron Scattering (SANS) and by no means is meant to be complete in the frame work of the Spring School. After a short introduction into general conformations of polymers which is independent of the monomer chemistry, thus generally applicable, we will summarize some structural models which describe the statistical properties of polymeric chains. Then we will develop some useful scattering approaches for mixtures of labelled and unlabelled chains, for linear and architecturally different chains. Details of the method of Small Angle Scattering are described at full length in the contribution by Frielinghaus (C1) and will not be repeated. Overall, this chapter tries to bridge the general text book science for linear polymers to more advanced and architecturally complex polymer structures in such a way that an appropriate base to facilitate the understanding of recent literature is provided. Therefore, the reader is made familiar with the access by scattering for the investigation of amorphous polymers, mostly in the melt state. A good introduction into general polymer physics is given in [1-7] and references therein. The connection to scattering methods is best treated in [8-11]. We warmly suggest these references for further lecture.

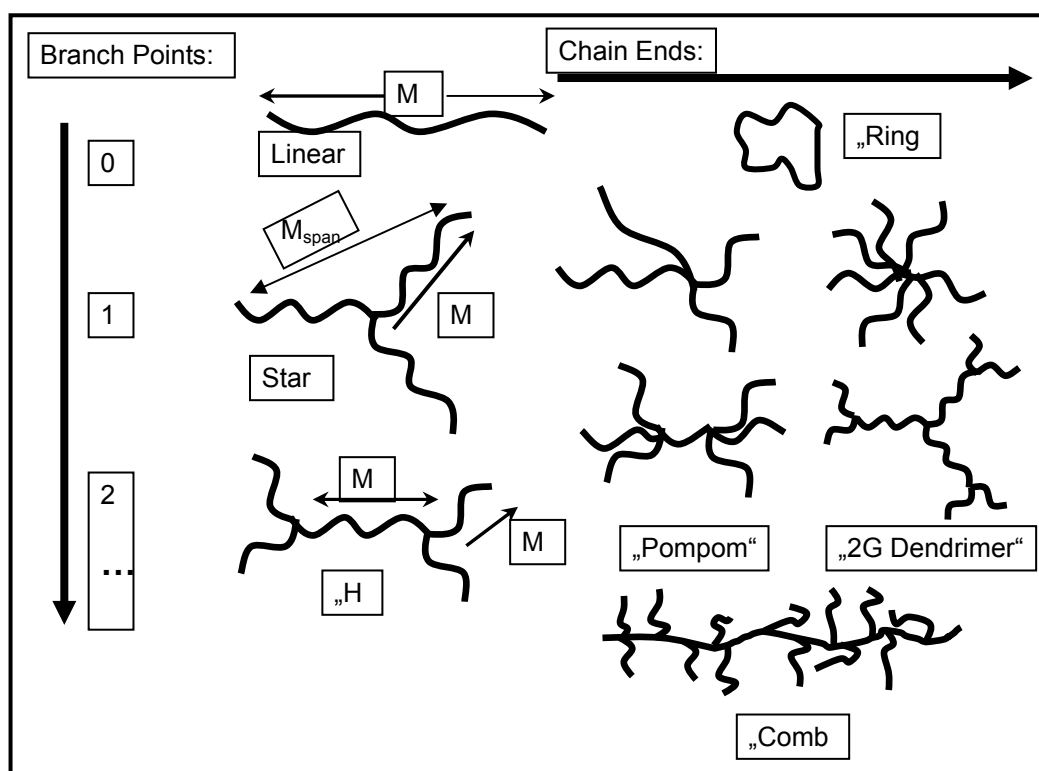


Fig. 1: Overview of most important architectural polymer structures as a function of the number of branching points. Of these, the linear and the star polymer represent basic building blocks for higher complex branched polymers.

2 Polymer Chain Models and Architecture

A polymer is a chain of several polyatomic units called monomers covalently bonded together. Since virtual all kinds of molecules can act as a monomeric unit, thereby only differing in the ways in which they can be bound together, a wealth of synthetic and naturally occurring polymers with enormous diversity in properties is nowadays known. We mention e.g proteins, DNA, glass, thermoplasts and rubber. They all belong to the class of polymers. Given their importance, an adequate description of model polymers has become a prerequisite. This brief summary serves to introduce the reader to some of the basic models with respect to scattering. The simplest descriptions of single-molecule models can then be expanded to branched polymers with some minor changes.

Polymers are often looked at like spaghetti-like or coiled molecules. Their stiffness varies from very flexible to rigid in the case of rods. Their configuration i.e their spatial distribution of segments changes all the time as the result of brownian dynamics which therefore leads to an enormous amount of possible configurations itself. The motion and dynamics of polymers will be discussed at full length in the session on polymer dynamics by Richter (E3). Here, we will stick to the determination and static investigation of their time-averaged structures.

To describe the statistical properties of such macromolecules, some variables need to be introduced. How can we calculate the size? For this, basic models were developed in the past

for linear chains with different levels of sophistication and approximations. We will summarize these only here in this chapter on the scattering of polymer chains in equilibrium and introduce at this stage also the corresponding length scales.

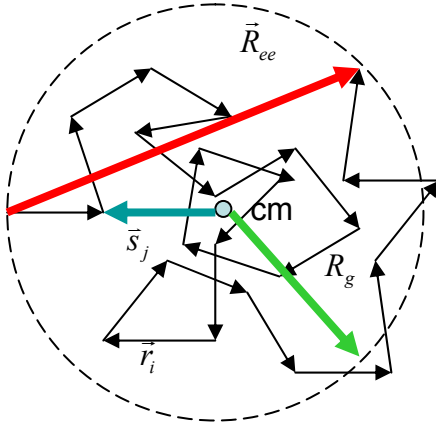


Fig. 2: A freely joined chain and definitions (see text).

The simplest model to deal with is the freely jointed chain (FJC). An example for such a configuration is shown in Fig. 2 and illustrates the idea that polymer chains are performing random walks. With this, the ensemble of systems can be characterized by average quantities. One is the so-called end-to-end vector.

$$\begin{aligned}\vec{R}_{ee} &= \sum_{i=1}^n \vec{r}_i \\ R_{ee}^2 &= \sum_{i,j=1}^n \vec{r}_i \cdot \vec{r}_j\end{aligned}\tag{1}$$

with R_{ee}^2 as the scalar quantity. The bond vector length (or step), connecting 2 atoms is l .

A further important parameter which has its counterpart in classical mechanics is the radius of gyration R_g :

$$R_g^2 = \frac{1}{n+1} \sum_{i=0}^n \vec{s}_i^2\tag{2}$$

where now the vectors $\vec{s}$ are the distance vectors with respect to the center of mass, R_{CM} with

$$R_{CM} = 1/N \sum_{i=1}^N r_i\tag{3}$$

Averaging over all conformations in both upper formulas leads for the case of a fully freely jointed chain to a mean squared end-to-end distance of

$$\langle R^2 \rangle = \sum_{i,j=1}^n \langle \vec{r}_i \vec{r}_j \rangle = nl^2 + 2 \sum_{i < j}^n \langle \vec{r}_i \vec{r}_j \rangle \quad (4)$$

whereas the average end-to-end distance $\langle R_{ee} \rangle = 0$ due to the ensemble average. With the Lagrange theorem a relation between $\langle r_{ij}^2 \rangle$ i.e. the squared distance between 2 scatterers i and j within the chain can be obtained. It states that

$$R_g^2 = \frac{1}{2(n+1)^2} \sum_{i,j}^n \langle (r_i - r_j)^2 \rangle = \frac{1}{2(n+1)^2} \sum_{i,j}^n \langle r_{ij}^2 \rangle \quad (5)$$

The calculation of the end-to-end distance which characterizes the full size of a chain i.e. it constitutes the diameter of a hypothetical sphere including the full chain, can now be performed for different chain models. The upper model of the FJC freely jointed chain assumes an equal probability in 3D of all bond vectors, random bond rotation angles while keeping the bond length constant. The orientation of each segment or bond is therefore independent of all others and as a consequence the 2nd term which is the scalar product in Eq. 4 averages out to zero. The mean radius of gyration can then be obtained from evaluating the double sum in Eq. 5 and using $r_{ij}^2 = (j-i)l^2$ - a result of random walk statistics - becomes

$$R_g^2 = \frac{1}{6} nl^2 \quad (6)$$

From both end-to-end distance and radius of gyration an important statement which applies to polymer chains in the bulk or theta state is already observed: the size depends on the square root of the number of basic steps, $\sqrt{n}$. This is a result which has its equivalent in the random walk statistics where now the position of the monomers is replaced by the trajectory of a randomly-diffusing particle and so the variable becomes the time, $\sqrt{t}$.

It is clear that the size or overall dimension of architecturally more complex branched chains cannot be estimated in the same way, basing on the end-to-end distances. This will involve a little bit different treatment as will be shown later.

However, real polymers are also not connected in this freely jointed way. Instead, bond angles assume well-defined values and correlations between bonds within the chain as well as from the environment will affect the size. Intuitively it can be understood that these correlations will vanish with increasing separation distance. Also, the flexibility of polymer chains is restricted by the fact that rotations with the so-called bond rotation angle φ_i are enabled within a certain range only due to steric reasons.

If we take the first FJC model as the reference then the difference to real polymers will be quantified in terms of a parameter which is denoted C_∞ . This is defined as

$$C_\infty = \frac{\langle R_{ee}^2 \rangle}{nl^2} \quad (7)$$

In the case of the random walking chain in the FJC, C_∞ is thus 1 per definition.

A first refinement is the case of the freely rotating chain model (FRC) in which now valence angles are restricted additionally but still torsional angles are left free to rotate. Then the flexibility parameter after some calculations becomes

$$C_{\infty} = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \quad (8)$$

which leads to values between 2 and 3 for the typical polymers. θ is the complementary angle between 2 bonds.

A further extension is the chain model with hindered rotation (HRC) which is better known as the rotational isomeric state model by Flory. This adds restrictions now also on the torsional degree of freedom. Instead, using the rotational barriers, a good estimate for allowed, energetically and sterically different configurations can be readily obtained. For C_{∞} , values considerably larger than 3 are found. Experimentally, the parameter as determined from small angle neutron scattering investigations is situated in the range between 3 and 10. We can summarize this by stating that highly-coiled polymers are characterized by low C_{∞} values whereas extended or loosely-coiled chains show, on the contrary, high C_{∞} .

The description of chain dimensions thus involves several steps. A summary of currently used length scales in the literature which are inherently connected to the random coil description and resolution therefore is at its place here. Various expressions found for the chain end-to-end distance are

$$\begin{aligned} \langle R_{ee}^2 \rangle &= C_{\infty} N_{\text{mono}} n_b l^2 \\ \langle R_{ee}^2 \rangle &= N_{\text{mono}} l_{st}^2 \\ \langle R_{ee}^2 \rangle &= N_{\text{Kuhn}} l_{\text{Kuhn}}^2 \end{aligned} \quad (9)$$

Here, n_b is the number of backbone bonds per monomer with rms bond length l , l_{st} is the statistical segment step length per monomer and l_{Kuhn} is the Kuhn segment step length. In the chain model of Kuhn [24], the correlation between bonds is taken into account so that the statistics of the FJC is retrieved for lengths larger than the Kuhn segment length. For this purpose, this effective segment length, l_{Kuhn} is introduced, which is related by $l_{\text{Kuhn}} = C_{\infty} l$. Likewise, $N_{\text{Kuhn}} = N / C_{\infty}$. The Kuhn segment is thus the minimum length scale above which a real chain behaves again like the freely jointed one. It further preserves the contour length with $l_{\text{Kuhn}} N_{\text{Kuhn}} = Nl$. Due to the direct comparison of molecular weights, provided by the synthetic chemists, with computations for the end-to-end distance, the definition of the statistical segment length per monomer is slightly more favoured whereas this is, however, no strict rule. This is also true for the following sections in this chapter on the scattering of polymers. Without going into detail and referring to more general literature [8], also a so-called persistence length l_p can be defined which is $2l_{\text{Kuhn}}$.

The distribution of the end-to-end vector is treated in many text books on statistical physics and will therefore not be repeated here. It shows that the distribution function $p(R)$ of *any* intramolecular distance follows a Gaussian distribution with

$$p(R, N) = \left(\frac{3}{2\pi \langle R^2 \rangle} \right)^{3/2} \exp \left(\frac{-3R^2}{2 \langle R^2 \rangle} \right) \quad (10)$$

3 Scattering: intra- and inter-chain contributions

3.1 The single-chain structure factor

A scattering volume contains many polymer chains, each with N scatterers i.e. monomeric units here and with a coherent scattering length b . Their density is not constant and shows random fluctuations around an average value. $n_i(r) = 1$ if the monomer of type i sits at r_i . We define $\langle n(r) \rangle = n = N/V$. The variation in the density is then $\Delta n(r) = n_i(r) - \langle n \rangle$. The static structure factor is defined as the density-density correlation function $\langle n(-q)n(+q) \rangle$. So, if in the system n_p chains, which all have N monomers with a scattering length b , are present the coherent scattering, i.e. the macroscopic differential cross section per unit volume, $\frac{d\Sigma}{d\Omega}(q) = \frac{1}{V_s} \frac{d\sigma}{d\Omega}(q)$ in $[\text{cm}^{-1}]$ and further short $I(q)$ can be calculated using:

$$I(q) = \frac{b^2}{V_s} \sum_{\alpha, \beta=1}^{n_p} \sum_{m, l=1}^N \langle \exp(i\vec{q}(\vec{r}_{\alpha, m} - \vec{r}_{\beta, l})) \rangle = \frac{b^2}{V_s} S(q) \quad (11)$$

In the double summations the indices m and l are the monomer numbers and symbol α and β are different chains. $r_{\alpha, m}$ is thus the position of the m -th monomer on chain α . This can be rewritten into 2 parts: i.e. the intra-chain scattering is due to the contribution from 2 monomers on the same chain and an inter-chain part arises in the case that both monomers are situated on 2 different chains. For the simplest case of a dilute dispersion, we can further assume

$$\langle \exp(iq(r_{\alpha, m} - r_{\beta, l})) \rangle = 0 \Rightarrow \sum_{\alpha, \beta} \dots \rightarrow \sum_{\alpha} = n_p \quad (12)$$

because the chains are sufficiently well separated in space and the phase factor from each chain will be completely uncorrelated. Then the contribution of the inter-chain term cancels out on average. This allows us to determine the single chain structure factor $S_l(q)$. We can then re-write Eq. 11 (n_p and double sum over α, β cancel) as

$$S_l(q) = \frac{1}{N} \sum_{i, j=1}^N \langle \exp(i\vec{q}(\vec{r}_{m, i} - \vec{r}_{n, j})) \rangle \quad (13)$$

We will come back to this in the context of the scattering of concentrated blends where inter-chain contributions have to be included in the full description. At this point it suffices to evaluate for pedagogical reasons the low q expansion. From this the radius of gyration which was introduced in the first part of this contribution, independent of the shape or structure can be determined. The Taylor expansion of the structure factor for $q \ll$ then yields

$$\begin{aligned}
NS(q) &= \sum_{m,l} \langle 1 + i\vec{q}(\vec{r}_m - \vec{r}_l) - \frac{1}{2}q^2 \sum_{m,l} (r_m - r_l)^2 + \dots \rangle \\
&= N^2 - \frac{1}{2}q^2 \sum_{m,l} \langle (x_m - x_l)^2 + (y_m - y_l)^2 + \dots \rangle \\
&\Rightarrow N^2 - \frac{1}{2}q^2 \sum_{m,l} \frac{1}{3} \langle (r_m - r_l)^2 \rangle + \dots \\
&= N^2 (1 - \frac{1}{3}q^2 R_g^2 + \dots)
\end{aligned} \tag{14}$$

using the former result for R_g . Eq. 14 clearly proves that the low angle limit of the structure factor always yields both N and R_g if we will come back to this result later.

3.2 The Debye function

We have stated that the Gaussian distribution is a very good approximation for the real chain statistics. Then this yields

$$\langle \exp(i\vec{q}\vec{r}_{ij}) \rangle = \exp(-1/2 \langle (q\vec{r}_{ij})^2 \rangle) = \exp(-1/6q^2 \langle r_{ij}^2 \rangle) \tag{15}$$

For the isotropic gaussian chain we find

$$\langle (x_i - x_j)^2 \rangle = \langle (y_i - y_j)^2 \rangle = \langle (z_i - z_j)^2 \rangle = \frac{1}{3}l_{st}^2|i - j| \tag{16}$$

This result can be used and Eq. 13 can be evaluated in the full q -range with

$$S_1(q) = \frac{1}{N} \sum_{m,l}^N \langle \exp(i\vec{q}(\vec{r}_m - \vec{r}_l)) \rangle = \frac{1}{N} \int_0^N dm \int_0^N dl \exp(-\frac{1}{6}q^2 l_{st}^2(m-l)) \tag{17}$$

Here, the discrete sum has been already replaced by the continuous integral form (for N large enough, typically $N > 80$) which is the basis for all further calculations in this manuscript chapter on polymer scattering. It is the basic result for Gaussian chains. Its strength will be shown on selected examples, covering the most important fields of current polymer investigations. The statistical segment length per monomer l_{st} is used in conjunction with the total number of monomers, m and l , given by N . This integral can be solved analytically. The form factor $P(q)$ is defined as $S_1(q)/N$ and in discrete form is

$$P(q) = \frac{1}{N^2} \sum_{m,l} \exp(-\frac{1}{6}q^2 l_{st}^2(m-l)) \tag{18}$$

For long chains ($N \rightarrow \infty$), $P(q)$ is called the Debye function $g_D(x)$ with

$$g_D(x) = \frac{2}{x^2} (\exp(-x) - 1 + x) \tag{19}$$

and the argument $x = (qR_g)^2$. A SANS experiment with fit to the Debye function is presented in Fig. 3 in a linear scale and in the form of a 2nd moment Kratky representation achieved when $g_D(x)$ is multiplied by q^2 . The Kratky representation emphasises the high q -regime. For Gaussian chains with an asymptotic q^{-2} behaviour the high q regime then assumes a plateau. As shown the data are in perfect agreement with the Gaussian chain results derived above.

Small and high q regimes can also be explicitly obtained from expanding Eq. 19 for $x \rightarrow 0$. For small q , we then have $g_D(x) \approx 1 - 1/3x + \dots = 1 - 1/3q^2R_g^2 + \dots$. Reversely, this is the Taylor equivalent of $\exp(-x)$, which can be conveniently plotted in either the Guinier representation $\ln(g_D)$ vs q^2 from which then the slope contains R_g , or in a Zimm plot i.e. the inverse structure factor $1/S(q)$ vs. q^2 . The disadvantage of the latter is that slope and intercept in the linearized form are coupled whereas they are independent in the logarithmic way. The low q expansion allows a fast determination of R_g . An ultra-fast single-point estimate of the chain dimension can be obtained as follows: for $q^* = 1/R_g$ it can be easily obtained then that the scattering intensity at q^* has dropped to $2/3$ of the forward scattering value at $q=0$. Thus, in the low q regime we obtain direct information on the chain molecular weight M_w (via N) and the radius of gyration R_g . For high q , Eq. 19 on the other hand gives

$$g_D(x) \approx \frac{2}{x} = \frac{2}{q^2 R_g^2} \sim \frac{1}{C_\infty} \quad (20)$$

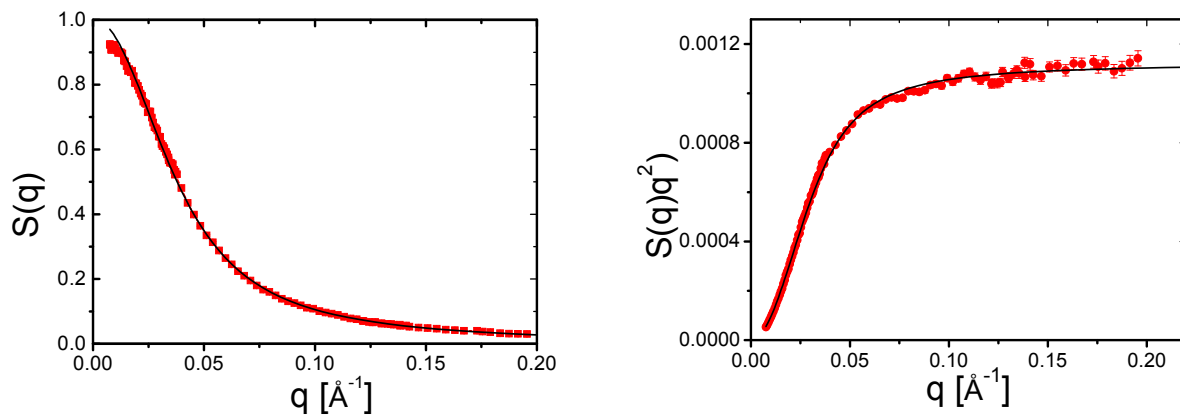


Fig. 3: Experimental scattering data, normalized to $S(q)$ on a poly-alkylene-oxide polymer, obtained at KWS2@FRM-2, Munich [15]. On the left, the Debye curve fits ideally, showing the Guinier region and the high q -dependence q^{-2} . On the right, the Kratky region is highlighted.

However, since data at high q , where the level of incoherent background (see D1) plays an important role, can be sensitively affected by erroneous subtraction, its use for the estimation of R_g is limited.

4 Blend of linear Polymers

4.1 Mixture of 2 polymers

The above applied to a general system in which the contrast was given by a polymer vs. a background with zero scattering length. This is not what one wants to measure nor is it generally the case. The power of the neutron scattering approach is the use of the natural contrast between protonated and deuterated components, i.e. where a label is able to provide

the structure of a polymer chain in the phase which scattered before incoherently as from a single phase. The total structure factor in a dense system is obtained from Eq. 11 and split into an intra-chain and an inter-chain part.

$$S(q) = MN^2P(q) + M(M-1)N^2R(q) \quad (21)$$

If we consider a mixture of 2 polymers with M chains, which are identical in length with N monomers and have no preferential interactions with each other, we define the form factor $P(q)$ and the inter-chain structure factor $R(q)$ which is sometimes even playing a dominating role. $P(q)$ has been defined before and $R(q)$ is formulated similarly with double sums:

$$P(q) = \frac{1}{N^2} \sum_{m,l}^N \langle \exp(iq(r_{1,m} - r_{1,l})) \rangle$$

$$R(q) = \frac{1}{N^2} \sum_{m,l}^N \langle \exp(iq(r_{1,m} - r_{2,l})) \rangle \quad (22)$$

The total structure factor then becomes (for $N_H = N_D$):

$$I(q) = \frac{1}{V_s} \sum_i^2 \sum_j^2 b_i b_j S_{ij}(q) \quad (23)$$

With for $i=H$ and $j=D$

$$S_{DD}(q) = M_D N_D^2 P_D(q) + M_D^2 N_D^2 R_D(q)$$

$$S_{HH}(q) = M_H N_H^2 P_H(q) + M_H^2 N_H^2 R_H(q) \quad (24)$$

$$S_{HD}(q) = M_D M_H N_H N_D R_{HD}(q)$$

With the incompressibility hypothesis one gets to

$$S_{DD} + S_{DH} = 0 \rightarrow S_{DD} = -S_{HD}$$

$$S_{DD} = -S_{HH} \quad (25)$$

We have implicitly assumed that the hydrogenous and deuterated polymers are identical and therefore exhibit the same intra-chain $P(q)$ and inter-chain structure factor $R(q)$, independent of the isotopic labelling. The inter-chain contribution can be expressed in terms of the intra-chain contributions which simplifies the scattering intensity to a rather simple expression in terms of a single chain contribution factor only.

$$I(q) = \frac{1}{V_s} (b_D^2 S_{DD}(q) + b_H^2 S_{HH}(q) + 2b_D b_H S_{HD}(q))$$

$$I(q) = \frac{(b_D - b_H)^2}{V_s} S_{DD}(q) \quad (26)$$

4.2 Mixture of 2 polymers in a matrix or solvent

The same reasoning as in the former blend can be done if it is mixed with a third component which may be e.g. a small scale solvent, a macromolecule, particle or a complex environment. Latter can consist of e.g. a hard confinement or aggregated nanoparticles or soft network.

Working through the equations one gets to a similar expression as for the simple symmetric blend with the exception that additional freedom or contrast can be provided. The contrast situation has been treated in detail in the scattering section (C1) and we refer to that. Taking into account that the medium in which the blend is embedded in, has a non-zero scattering length b_0 , the blend can be mixed as to obey

$$b_0 = xb_D + (1-x)b_H \quad (27)$$

provided b_0 takes a value between both constituent polymers with volume fractions x and $1-x$. It can itself be a mixture of e.g. different solvent molecules that do not show a coherent structure on the length scale of the macromolecules itself or e.g. also a random co-polymer with matched scattering length length. The full coherent intensity becomes

$$\begin{aligned} I(q) &= \frac{1}{V_s} ((b_D - b_0)^2 S_{DD}(q) + (b_H - b_0)^2 S_{HH}(q) + 2(b_D - b_0)(b_H - b_0)S_{HD}(q)) \\ &= \frac{1}{V_s} [(b_D - b_H)^2 x(1-x)M_D N_D^2 P_D(q) + (xb_D - (1-x)b_H - b_0)^2 S_{TOT}(q)] \end{aligned} \quad (28)$$

where we have substituted the appropriate form factors already. Eq. 28 shows different possibilities which can be advantageous and which are applied in several approaches, at least qualitatively. We notice that the single chain form factor of the blend can still be measured if

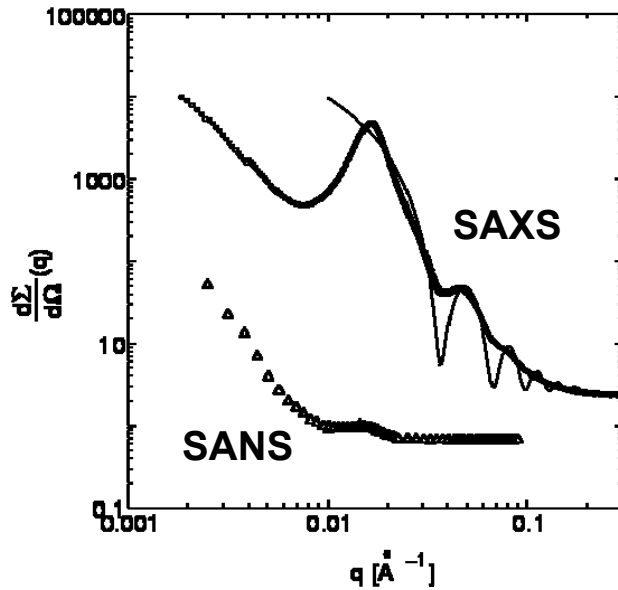


Fig. 4: Experimental phase matching: the scattering for neutrons is almost extinguished whereas xrays show the phase structure, i.e a cylindrical polystyrene mesophase domain inside a sea of polyisoprene arms [unpublished, PhD Thesis A. Botti, Univ. of Münster, 2001].

the 2nd term is known or is matched out. The contrast matching can be achieved if the blend is compositionally mixed so that the contrast factor is zero. The scattering length of the 3rd component or medium b_0 itself can be an effective one if e.g. solvent molecules are used which can be adjusted as to cope with the composition. Eq. 28 has another consequence: if

both polymers have the same scattering length, the 1st term vanishes and the intensity is given by the contrast with the medium. The 2nd term simulates a system in which all components have the same scattering length $\langle b \rangle$ and thus concentration fluctuations of the polymer become visible. This is the situation which is present if the probe is not neutrons but x-rays. Likewise, the first term also disappears if the mixture consists of only 1 single type of polymer! Latter is the direct equivalent of the ray study. Now the phase in which the polymer is can be studied. S_{TOT} corresponds then to e.g. the nanocomposite structure or the network-like environment. An example is given in Fig. 4. We note that, still using the same incompressibility rules, Eq. 28 can be re-casted such that then the 3 different diagonal structure factors, i.e S_{HH} , S_{DD} and S_{TOT} occur.

4.3 The dilute solution

To be complete we mention only the case of dilute polymer solutions. For low concentrations of labelled species in one of the components, Zimm has proposed an effective single contact model. If 2 monomers on closeby chains interact, their coordinates can be distributed in the interchain structure factor like

$$\sum_{ij}^N \langle \exp(iqr_{1i2j}) \rangle = \sum_{ij}^N \langle \exp(iqr_{1i1k}) \rangle \langle \exp(iqr_{1k2m}) \rangle \langle \exp(iqr_{2m2j}) \rangle \quad (29)$$

The middle term is the excluded volume between both polymer chains.. If this is substituted in $R(q)$ and terms are reorganized, Zimm derived that

$$R(q) = -2A_2M^2P^2(q) \quad (30)$$

A_2 is the 2nd virial coefficient. The famous Zimm equation follows :

$$\frac{Kc}{I(q)} = \frac{1}{M_w P(q)} + 2A_2c + \dots \quad (31)$$

We will not go into details in the use of this equation which was significantly used in the last decades for the determination of polymer chain structure and polymer-solvent interactions and we refer to some specialized literature. For blends its use has been marginal and for these the high concentration method is more favoured. It can be seen from the functional form in Eq. 31 that the single chain information can be extracted from extrapolation to $c=0$ whereas the 2nd virial coefficient can be derived involving the extrapolation of $P(q)$ to $P(q=0)$ where this is by definition =1.

4.4 Mixture of 2 polymers with interaction

In the former 2-component mixture, polymers behaved ideal, did not interact much and especially were symmetric. For asymmetric systems, one obtains the result in Eq. 32 which is identical to that obtained from a complicated random phase approximation (RPA) by Leibler [12] which applies to a general mixture of 2 asymmetrical polymers that differ only in their isotopic labelling and possibly interact. In the classical approach the Flory-Huggins interaction parameter is therefore set to $\chi = 0$. We get

$$S(q) = \frac{M_H N_H^2 P_H(q) M_D N_D^2 P_D(q)}{M_H N_H^2 P_H(q) + M_D N_D^2 P_D(q)} \Rightarrow \left[\frac{1}{S_{0HH}(q)} + \frac{1}{S_{0DD}(q)} - 2\chi_{HD} \right]^{-1} \quad (32)$$

The index 0 now means that we deal only with the bare correlation functions assuming no interaction between the chains and is not to be mixed up with $S(q)$. S_{0HH} (and S_{0DD} similarly) is defined as $\phi N_H g_D(N_H)$. ϕ is the respective volume fraction in the mixture. The χ parameter is strongly temperature dependent. For a mixture of 2 polymers, by incompressibility the cross term S_{0HD} is zero. In the random phase approximation the chains are nearly ideal and perform random walks. The full RPA treatment (Eq. 33) and the consequences becomes clear if the mixture is replaced by e.g. a tri-block copolymer. It can be shown by exercise that the simple mixture can be retrieved by substituting the appropriate function into the partial structure factors. The RPA approximation thus effectively accounts for the role of the inter-chain contributions.

5 Tri-block copolymers: an example for RPA

The random phase approximation (RPA) can be used for interacting systems and was originally developed by P.G. De Gennes. If different chemistries come together, also different interactions can be expected and therefore phase separating mechanisms can get active. Even the exchange between H and D can be sufficient. Since scattering is just sensitive to fluctuations in the composition, it is therefore very often used to study phase diagrams. Let us consider here the scattering of a symmetrical tri-block copolymer structure, consisting of identical monomers but differing only in their scattering length. We assume ideal mixing, thus negligible contributions from the Flory-Huggins parameter χ . We refer to the literature for more general treatments in isotopic block copolymers or even general block copolymers of different chemistries which then lead to micro-phase separation and meso-phases. They are discussed in the section on the SANS technique. The present example treats a HDH tri-block with a total of N monomers with N_H resp N_D monomers in the separate blocks of which the central block is deuterated. Then the problem reduces to the calculation of the partial structure factors which is done similar as we did to obtain the Debye function g_D .

These are fed into the general RPA equation, Eq. 33 which can re-organized to highlight the different contributions

$$\begin{aligned} S_{RPA}(q) &= \frac{S_{0DD}(q)S_{0HH}(q) - S_{0HD}^2(q)}{S_{0DD}(q) + S_{0HH}(q) + 2S_{0HD}(q)} \\ &= S_{0DD}(q) - \frac{(S_{0DD}(q) + S_{0DH}(q))^2}{S_{0DD}(q) + S_{0HH}(q) + 2S_{0HD}(q)} \end{aligned} \quad (33)$$

We here explicitly assumed no interactions and near-ideal Gaussian chains. f is the fraction of the i th monomer type in the tri-block, $f = N_i/N$ and N_i is the number of segments in the block. Performing the calculations leads to new correlations which are absent for a mixture of simple linear polymers by adjusting the limits of the integration:

$$\begin{aligned}
S_{0H...H}(q) &\rightarrow \int_0^{N_H} \int_{N_H+N_D}^N = \left(\frac{1 - \exp(-q^2 R_{gH}^2)}{q^2 R_{gH}^2} \right)^2 \exp(-q^2 R_{gD}^2) \\
S_{0HD}(q) &\rightarrow \int_0^{N_H} \int_{N_H}^{N_H+N_D} = \left(\frac{1 - \exp(-q^2 R_{gH}^2)}{q^2 R_{gH}^2} \right) \left(\frac{1 - \exp(-q^2 R_{gD}^2)}{q^2 R_{gD}^2} \right)
\end{aligned} \tag{34}$$

Here, R_{gD} resp R_{gH} are defined as $\sqrt{f} R_g$ resp $\sqrt{(1-f)/2} R_g$ in view of the gaussian character (remember the N-dependence of the end-to-end distance!). It can be easily seen that the RPA for the tri-block can be simplified back to the limiting case of a linear chain without labeled wings by letting the wings $\rightarrow 0$. Also, the RPA of the tri-block can be easily converted and transformed to the case of a general di-block copolymer by dropping the non-bonded $H...H$ correlation term.

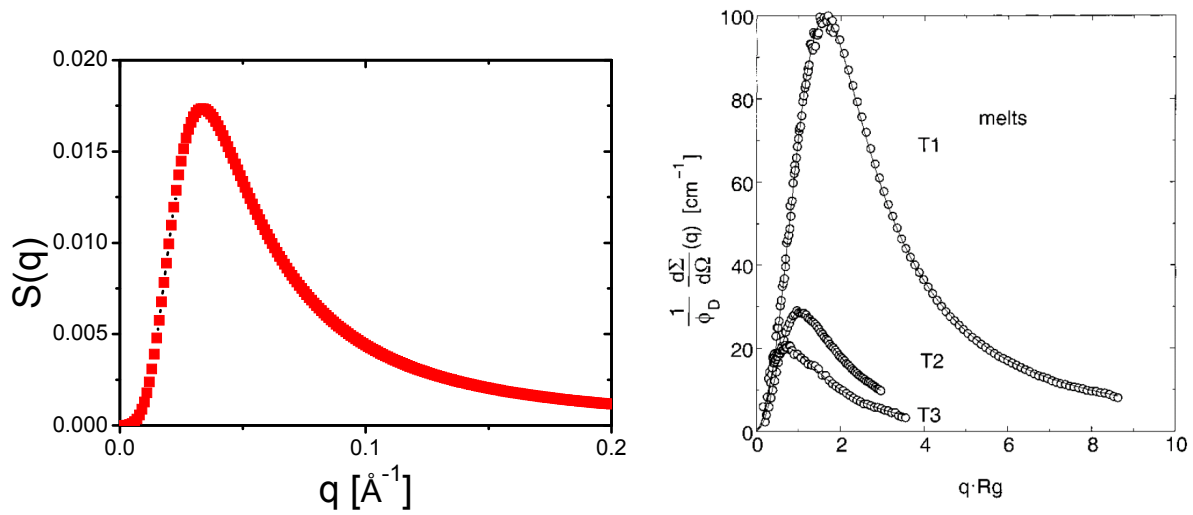


Fig. 5: Computational example for a tri-block scattering with $R_g \sim 90 \text{ \AA}$ (left) and on the right an experimental system obtained at KWS1@FRJ2, Jülich with fits to 3 different tri-blocks differing only in the middle block length in reduced representation using R_g of the center block [13]. Reprinted with permission from *Macromolecules*, **34**, 2186(2001). Copyright (2001) American Chemical Society.

Eq. 33 nicely illustrates that the scattering is dominated by 1 block. As an example we choose the D block. For an isolated polymer with the length N_D one expects a Debye-like curve. However, the 2nd term in eq 33 contains the correction to this due to the connectivity of this block now into a tri-block. The connectivity leads to the subtraction of the 2nd term and leads to a pronounced peak in the scattering intensity. The peak intensity and position is determined by the center block and the interaction parameter χ (if any) leading to stronger peaks close to (micro-)phase separation. This is the correlation hole effect. At $q=0$ there are no composition fluctuations as on this length scale the same fluctuations as inside the molecules occur. For intermediate q the largest fluctuations occur around $q \sim 1/R_g$ of a branch and for even larger q there is no difference between a blend of unconnected blocks and the block copolymer. The

dependence is again that of the random walk. If this tri-block is mixed with a linear chain which has the scattering length in common with one of the blocks, the respective contributions are weighed with the volume fraction in the blend and added to the respective partial structure factors. This leads to new composition fluctuations at low q . In the original work by Leibler it is even shown that due to sometimes just polydispersity in the block copolymer, be it in the total length, or in the block length or composition, also a non-zero intensity is expected. Using the special anionic polymerization technique which guarantees very narrow molecular weight distributions and low polydispersities well below 1.1, this can be very well avoided as shown in the example from our lab (Fig. 5) and the analysis is a strong measure of quality of the synthetic efforts.

6 Branched Chains

6.1 The branching parameter g

There are many different architectures in branched chains. A summary of the most prominent ones which can be synthesized by the mentioned method of anionic polymerization as model systems are shown in Fig. 1. There, e.g. a star-branched chain consists of a core and arms of a more or less similar length. Therewith, a two-arm star polymer is essentially a linear polymer. A comb polymer, on the other hand, consists of a linear-chain backbone and many combs or teeth that stick out from functional groups distributed somehow along the backbone. These junctions or main-chain branching points may be uniformly or randomly spaced. The comb length can be highly uniform depending on the synthesis route. Comb polymers with uniform distribution of branching points and a uniform distribution of branching length can be made with special techniques and low yields only. Branched chains where branching points are distributed randomly, are much more common, however. Branches may have also further branches, leading to higher generations. Then the longest chain i.e. the backbone in the random-branched chain with the span molecular weight, can hardly be distinguished anymore. The length of the branches divides these systems then in long-chain branched and short-chain branched polymers. Long-chain branching reactions can be induced already in special chain-reaction polymerization methods. If the frequency of branching is high, then the chain becomes hyper-branched. This is another class. E.g. in a dendrimer shown in Fig. 1, every repeating unit is trifunctional. Starting at the center, the number of segments or branches in a layer or generation increases by a factor of 2 in the next generation.

The best quantity to characterize the overall dimension of a branched chain is through the radius of gyration, R_g . An end-to-end distance cannot be uniquely identified anymore for non-linear chains and instead, a branching parameter g is defined as

$$g = \frac{R_{gb}^2}{R_{gl}^2} \quad (35)$$

where R_{gb}^2 now is the mean squared radius of gyration for the branched chain, and R_{gl}^2 is the mean square radius of gyration for the linear chain. The ratio is calculated for the two polymers of the same molecular weight. It can be easily seen in Fig. 1 that branching concentrates monomers around the center of mass. Therefore, $g \leq 1$ always. As an example we calculate here g for an n_A -arm star polymer. With some more efforts and approximations

the branching factor of more complex architectures can be obtained similarly. We assume that each arm behaves as an ideal chain and has the same number of monomers, N_l ($N_l \gg$). Let $\vec{r}_{ij}$ be the position of the j th monomer ($j:0 \dots N_l$) on the i th arm ($i:1 \dots n_A$), as illustrated in Fig. 6. With Eq. 5, the mean-squared radius of gyration R_{gb}^2 is expressed as

$$\begin{aligned} R_{gb}^2 &= \frac{1}{2n_A^2 N^2} \sum_{i,n=1}^{n_A} \sum_{j,m=1}^{N_l} \langle (r_{i,j} - r_{m,n})^2 \rangle > \\ &= \frac{1}{2n_A^2 N^2} \sum_{i=1}^{n_A} \sum_{j,n=1}^N \langle (r_{ij} - r_{in})^2 \rangle + \sum_{i \neq m}^{n_A} \sum_{j,n=1}^N \langle (r_{ij} - r_{mn})^2 \rangle > \quad (36) \\ &= \frac{1}{3} b^2 n_A N(N+1)(3n_A N - 2N - 1) \end{aligned}$$

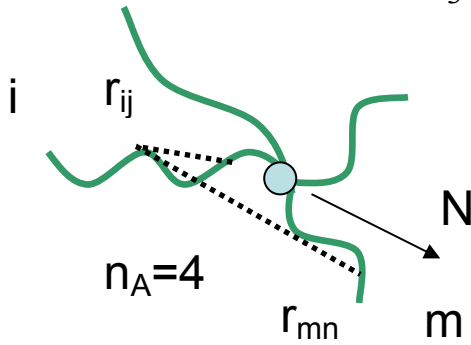


Fig. 6: Definitions of coordinates for a symmetric 4-armed star polymer

The mean squared monomer distance is calculated for monomers on the same arm and those on different arms separately. For large enough N we obtain

$$R_{gb}^2 \cong b^2 \frac{N}{n_A} \left(\frac{1}{2} - \frac{1}{3n_A} \right) \quad (37)$$

Again, to prove the consistency the limiting case of the linear polymer is well suited. Linear polymers can be looked at as 2-arm stars or even as 1-arm star objects. As one can easily verify, the known relation for R_g coming from the FJC model is obtained. Thus, with this the branching parameter g is a nice descriptor for branching.

$$\begin{aligned} n_A = \{1,2\} &\rightarrow R_{gl}^2 = \frac{Nb^2}{6} \\ g &= \frac{1}{n_A} \left(3 - \frac{2}{n_A} \right) < 1 \end{aligned} \quad (38)$$

6.2 Form factor of a symmetric star polymer

We can now calculate the form factor $P_{\text{star}}(q)$ for this n_A -arm star polymer with this uniform arm length N_l . When calculating the average of $\exp(i\vec{q}(\vec{r}_m - \vec{r}_n))$, it is again necessary to distinguish between the two cases for r_m and r_n i.e. both on the same arm and both being on

different arms. The former case takes place with a probability of l/n_A and obviously $(1-l/n_A)$ for the other. Then,

$$P_{star}(q) = \frac{1}{n_A} \langle \exp(iq(r_m - r_n)) \rangle_1 + (1 - \frac{1}{n_A}) \langle \exp(iq(r_m - r_n)) \rangle_2 \quad (39)$$

where the subscripts 1 and 2 correspond to the two cases. The averages are taken with respect

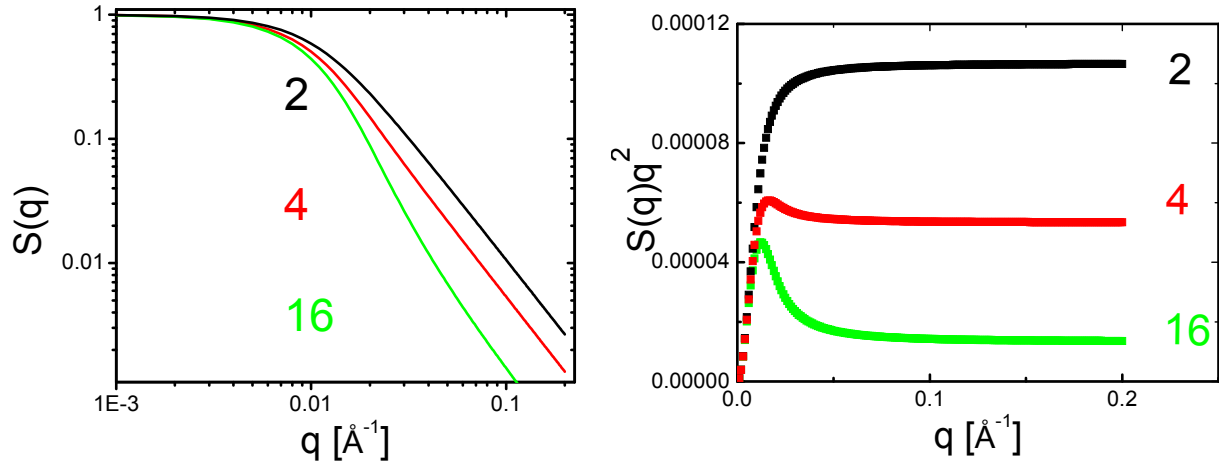


Fig. 7: Star scattering: log-log and Kratky representation for stars with same number of monomers but varying functionality, going from 2 to 16. The results show clearly that for $n_A=16$ the scattering starts to resemble that of spherical objects from the apparent q^{-4} dependence below $q=0.02\text{\AA}^{-1}$.

to the two monomers over the length of the arm. The second average can be approximated after some manipulation to consist of the independent averages of single arms as

$$\begin{aligned} \langle \exp(iq(r_m - r_n)) \rangle_2 &\approx \langle \exp(iq(r_m - r_0)) \rangle^2 \\ \langle \dots \rangle_2 &= \left[\frac{1}{N_l} \int_0^{N_l} dn \exp\left(-\frac{1}{6} q^2 n l_{st}^2\right) \right]^2 = \left[\frac{1 - \exp(-q^2 R_{g,l}^2)}{q^2 R_{g,l}^2} \right]^2 \end{aligned} \quad (40)$$

Combining all results leads to the form factor of a star polymer with n_A arms and radius of gyration per arm $R_{g,l}$ with N_l monomers

$$P_{star}(q) = \frac{1}{n_a^2 N} (n_a N^2 g_D(N) + n_a (n_a - 1) \left[\frac{1 - \exp(-q^2 R_g^2)}{q^2 R_g^2} \right]^2) \quad (41)$$

6.3 Form factor of a ring polymer

Ring polymers are very interesting macromolecules in that they differ structurally and dynamically from the typical linear polymers due to the total absence of chain ends that are dominating for the dynamics in the melt. They have become of renewed interest in the last years due to the synthetic efforts in producing linear contaminant-free ring structures while

minimizing concatenation reactions. As Fig. 8 shows, there are 2 different ways to define the intra-chain correlation between two monomers i and j . Both ways are equally probable and the occurrence is taken into account by multiplying the probabilities of selecting each different path. For the mean-squared distance between 2 monomers and the corresponding form factor we obtain then in analogy with the linear chain and including the closure relation

$$\begin{aligned} \langle r_{ij}^2 \rangle &= b^2 |i-j| \left(1 - \frac{|i-j|}{n}\right) \\ \rightarrow P(q) &= \frac{1}{n^2} n \sum_{i,j} \exp\left(-\frac{q^2 b^2 |i-j|}{6} \left(1 - \frac{|i-j|}{n}\right)\right) \end{aligned} \quad (42)$$

The single chain structure factor differs in a sensitive way from the pure linear curve as can be seen in Fig. 8. It leads to a peaked structure in the Kratky representation. This expresses the similarity of a ring polymer with a star or branched polymer (Fig. 7). The monomers of a ring are on average located at closer distance to the center of mass than in a linear chain, so an enhancement of the compacticity of the structure can be expected. The peak arises due to the increased correlation through the closed cycle and is therefore related to R_g of the ring. Latter can be calculated to be smaller than the linear by $\sqrt{2}$.

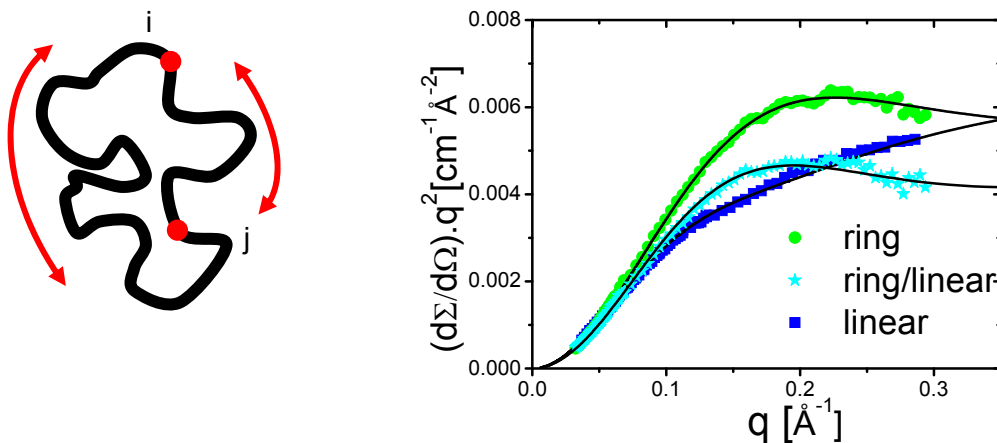


Fig. 8: Ring scattering: 2 possible ways to define the distance r_{ij} . Kratky representation to highlight the difference in the structure due to ring closure. In the ring/linear mixture the peak shifts to lower q and indicates a swelling of the ring conformation by penetrating linear chains. Adapted from [14].

7 Summary

We have discussed in a nut-shell various possibilities to investigate the structure of model polymeric chains in various environments and constitutions, some in more detail than others while keeping the focus on dense, amorphous and well-mixed systems. Mixtures of chemically different polymers behave much more complicated, are partly treated in other lectures and can be very well studied as well by the small angle xray scattering method. We have tried to summarize here only the most important concepts of the statistical structure of

ideally monodisperse chains and we have demonstrated how the particular structure affects the scattering behaviour. This text should be a basis in order to be of help in calculating more complex structures which are built up from the here discussed basic entities i.e the linear and the star polymer. It was a general aim thus to provide some useful basics which can be transferred to related sample systems.

Appendix

We had defined the macroscopic differential cross section $\frac{d\Sigma}{d\Omega}(q)$ per unit volume in $[\text{cm}^{-1}]$ as $\frac{1}{V_s} \frac{d\sigma}{d\Omega}(q)$. Here, V_s is the irradiated sample volume. In this context, another very often

used parameter, i.e. the scattering length density (or SLD), ρ , can be defined which replaces the scattering length b . This SLD or ρ is defined as $\sum_i b_i / V_0$ with V_0 a reference volume over

which the scattering lengths b are summed up and normalized to its volume. For polymers, V_0 typically is the monomeric volume and for simple molecules or particles it can be the sum of all the constituents. With this the intensity becomes

$$I(q) = \frac{N_p}{V_s} N^2 V_0^2 \rho^2 P(q) = \frac{N_p}{V_s} V_p^2 \rho^2 P(q) \quad (43)$$

With the relationship $N_p / V_s = \phi / V_p$ and V_p and ϕ being the polymer or particle molecular volume and volume fraction, this can be further simplified. An expression for SANS intensities which is often encountered, especially among experimentalists is then found as

$$I(q) = \phi V_p \Delta \rho^2 P(q) \quad (44)$$

Here, $\Delta \rho^2$ represents the contrast factor i.e. the squared difference between the scattering length densities of both components.

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