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SMALL ANGLE NEUTRON SCATTERING BY POLYMER SOLUTIONS

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1. INTRODUCTION

In certain conditions, a well collimated beam falling on a sample produces scattering close to the incident direction^[1]. This small angle scattering reveals correlations at large distances inside a sample, as typically exhibited in polymer solutions. Earlier the small angle scattering by polymer solutions was measured using electromagnetic radiations. In that case experiments were performed in dilute solutions for the purpose of polymer characterization^[2]. Small angle neutron scattering (SANS) is an experimental technique introduced since about ten years for the observation of the polymer conformation in all the concentration range from dilute solution to the melt^{[3][4][5][6]}.

In what follows, we will mainly be concerned with results obtained with this technique. Theoretical predictions will be used to interpret these results^{[7][8]}. After a brief recall (Section 2) of the elementary relations between scattering amplitude, index of refraction and scattered intensity, we will discuss in detail two concepts related to this last quantity: the contrast, derived in section 3 and the pair correlation function (section 4).

Experimental results obtained by SANS have been extensively reviewed in many general articles^[9]. We have limited our review to atactic polystyrene^{[6][10][11]} (and sulfonated polystyrene) in solution. This polymer is taken as a prototype of the flexible coil. As an example of a problem studied by SANS, we consider polymer coil shape as a function of polymer concentration. Using light or X-rays, experimentations could only observe the coil configuration in dilute solutions. But with use of neutron scattering, investigation of the coil configuration in other environments such as semi dilute and concentrated solutions become possible. We briefly recall the findings of the SANS by semi dilute polymer solutions:

- 1) Neutron, light scattering and osmotic pressure data could all be interpreted in terms of a single length ξ ^[16].
- 2) Characteristic domains of variation were found in the temperature concentration diagram^[17].

Results are mostly expressed in terms of power laws^{[14][15]}. A major experimental problem is to determine the characteristic exponents^[13] and the spatial range over which a given power law holds true (cross overs)^[53].

Another typical problem investigated by SANS is the nature of strong polyelectrolyte solutions. The scattering pattern is similar to the one

associated with a long range ordered structure. However experimentators are more and more convinced that the correct interpretation leads to a disordered structure.

In all these examples the polymer chain is in the equilibrium state. This state has been extensively studied since last ten years. A new problem is now the study of polymer conformation in non-equilibrium state, for example the stretched polymer chain. Neutron scattering in real experimental conditions are difficult because the scattered intensity is very low. The development of these studies request a new experimental approach. One is described in section 4.

2. ELEMENTARY RELATIONS

The scattering experiment analysis is based on elementary relations

2.a) The scattering amplitude by the elementary particle [8]

In the case of (High) polymers, the elementary particle is taken to be the monomer. The scattering amplitude by an isolated monomer is

$$a = \lim_{k_0 \rightarrow 0} \frac{m_n}{2\pi \hbar^2} \langle k_0 \hat{z} | T | k_0 \rangle \quad (1)$$

for the neutron radiation. Here \vec{k}_0 is the incident wave vector, \hat{r} is the unit vector pointing in the scattering direction, m_n is the neutron mass and T is the operator associated with the scattering [18].

The scattering amplitude by the electromagnetic radiation [19] will be defined by

$$a = k_0^2 \alpha \quad (2)$$

where α is the polarizability (Rayleigh scattering) and by

$$a = r_e Z \quad (3)$$

where r_e is the classical radius of the electron and Z the effective number of scattering electrons (Thomson scattering, X-ray [20]).

The differential scattering cross section for the single collision of the radiation with the elementary particle is then

$$\Sigma = |a|^2$$

2.b) Scattering amplitude and index of refraction

The index of refraction and the index of refraction increment at

constant volume, or at constant pressure, are observables from which the scattering amplitude can be determined.

Refraction is a result of multiple scattering. For a system of N elementary particles the index of refraction n is [19]

$$n^2 - 1 = - \frac{4\pi}{k_0^2} \frac{N}{V} a \quad (4)$$

If the sample is made of $\alpha = 1, \dots, m$ component with N_α elementary particles we get

$$a_\alpha = - \frac{k_0^2}{2\pi} n V \left(\frac{\partial n}{\partial N_\alpha} \right)_{\{N\}, V} \quad (5)$$

where the notation [8] for the subscript indicates that the quantity n has to be taken as a function of the set $\{N\}$ and the volume V .

This formula holds true for neutron scattering as well as light scattering. More precisely we would need to consider the states of polarization of the in- and out coming beam. Although such considerations are very important, we shall ignore them here.

2.c) Scattering amplitudes and scattered intensity

The result of a small angle scattering experiment with any radiation of wavelength λ can be described by the scattering vector $\vec{q} = \vec{K} - \vec{K}_0$ where \vec{K}_0 and \vec{K} are respectively the in- and out coming wave vectors. In small angle scattering we are only interested in elastic coherent scattering process, then

$$|\vec{q}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (6)$$

where θ is the scattering angle.

Neutron wavelengths available from cold sources in nuclear reactors, range from 2 \AA to about 15 \AA [21]. In that case values of the scattering vector q bridge the gap between the light scattering and classical X-ray scattering, and are matched to the molecular dimensions encountered in polymer physics (from some Angströms to some thousand Angströms).

This point out one advantage of the neutron scattering technique. It allows the measurement of the size of the polymer coil in the so-called "Guinier" range, as in light or X-ray scattering experiment^[20].

$$qR_G < 1 \quad (7)$$

where R_G is the radius of gyration of the coil, and also the monomer-monomer correlation function in the so-called "intermediate" range

$$R_G^{-1} < q < l^{-1} \quad (8)$$

where l is the step length.

But the striking advantage of this technique is given by the contrast between interaction parameter a (eq. 1) with various nuclei belonging to the molecules in the sample. For the electromagnetic radiation, the interaction parameter a (eq. 2 and 3) also varies with molecular specie. But the variation is less significant than in the case of neutrons.

For instance, with neutron radiation the parameter a can be negative as well as positive. This yields a considerable change, which is the basis of the SANS experiment for the investigation of polymer solutions and melts.

A particular feature in neutron interaction with nuclei, is the dependence of the interaction parameter a with the spin state of the neutron and the nuclei. This gives rise to an incoherent isotropic scattering, which is a background on which the coherent scattering is superimposed.

The scattering amplitude by a sample of N particles is, in the single collision approximation

$$A(\vec{q}) = a \sum_{j=1}^N e^{i\vec{q} \cdot \vec{r}_j} \quad (9)$$

where \vec{r}_j is the position of the j th particle. The coherent elastic scatter-

ring cross section is

$$\Sigma(q) = |\Delta(q)|^2 \quad (10)$$

and the scattered "intensity" measured by the detector

$$I(q) = C [\Sigma(q) + \Sigma_i] \quad (11)$$

where C is a constant depending of the diffractometer specifications. When C is a known quantity, the measurement is "absolute". Σ_i is the background, mainly due to the incoherent scattering.

If we are able to subtract from equation (11) the incoherent background, then the result contains all the physical information about the structure of the sample. It is written as

$$\Sigma(q) = K S(q) \quad (12)$$

where S(q) is the Fourier transform of the pair correlation function of the scattering particles, and K the contrast factor, which does not depend on the scattering vector. It measures the ability of the radiation to "see" the "solute" against the "solvent" background. Clearly the larger is this value, the more intense is the scattering.

3. THE CONTRAST

3.a Contrast length

Every polymer sample used in Small Angle Scattering experiments is a mixture of several components. How one particular component can be discerned among the others is given by the contrast between components. The contrast is described by a parameter, the contrast length b, whose value depends on the radiation used. The square of this length is the contrast factor K [22].

One part of the interest of the use of neutron beams in polymer physics is based on this term. This is due to the nuclear nature of the neutron-matter interaction. As pointed out in the above section, this interaction is measured by the coherent scattering length a. This parameter has been measured for all

elements [23]. Values for some chemical elements are listed in table I, together with the incoherent cross section.

TABLE I
Coherent scattering length and incoherent cross section for some atoms [23]

atom	isotope	$a_{\text{coh}} (10^{-12} \text{ cm})$	$\sigma_{\text{inc.}}$
Hydrogen	^1H	- 0.374	79.7
	^2D	0.667	2.2
Carbon	^{12}C	0.665	~ 0
Nitrogen	^{14}N	0.940	0.3
Oxygen	^{16}O	0.580	~ 0
Sulphur	^{35}S	0.284	~ 0

There is a very large difference between the scattering length of hydrogen ($a_{\text{H}} = - 0.374 \times 10^{-12} \text{ cm}$) and deuterium ($a_{\text{D}} = 0.667 \times 10^{-12} \text{ cm}$). Therefore the replacement of a hydrogen atom by deuterium is a major modification to the scattering, but does not markedly influence the thermodynamic properties of the molecule. So it is possible to modify the contrast of a given system, by dividing the homogeneous part into labeled (i.e. deuterated) and non labeled part. The homogeneous part can be the solvent, the solute or both. This is the basis of all experiments using the contrast variation method (see paragraph 3d).

The interaction of electromagnetic radiations (light or X-ray) does not exhibit such dramatic variations, and experiments are less fruitful as we will see below.

Contrast lengths are essential quantities in the interpretation of the small angle scattering experiment by multicomponent systems. The derivation of these lengths depends essentially on the definition of the

scattering experiment. In the following it is not intended to give any detailed derivation of these quantities but rather to introduce the basic equations and concepts which are used in SANS [8].

3.b Simple model

We assume that the scattering is produced by a fixed number of elementary particles filling a fixed volume. For a single component system, this model yields zero scattering. For a multiple component system, this model yields a finite scattering cross section. The derivation of the cross section is straightforward, but the above assumptions are somewhat particular. We will follow the derivation given in reference [24].

In order to make calculations easier the following assumptions will be made :

- i - the scattering medium is incompressible
- ii - the volume V does not depend on composition of the mixture.

Such a system can be viewed like a lattice, each lattice point being occupied either by a solvent molecule or by a monomer of the polymer molecule. To be more general we can say that each lattice point is occupied by one molecule of specie α ($\alpha = 1, \dots, m$). The number N_α of α molecules is fixed and the number of sites is $\sum_\alpha n_\alpha N_\alpha$ where n_α is the number of monomer for one α molecule. The volume of one monomer is v_α .

The total concentration of α monomers is given by $n_\alpha N_\alpha / V$ and the local concentration is

$$C_\alpha(\vec{r}) = \sum_{\alpha \in \alpha} N_\alpha \sum_{j \in \alpha}^{n_\alpha} \delta(\vec{r} - \vec{r}_{ja})$$

where \vec{r}_{ja} is the position of the j^{th} monomer of a molecule α belonging to the specie α .

Condition i) is written as

$$\sum_{\alpha=1}^m v_\alpha C_\alpha(\vec{r}) = 1 \quad (13)$$

the Fourier transform of the local concentration is expressed as

$$\tilde{C}_\alpha(\vec{q}) = \int_V d^3r e^{i\vec{q}\cdot\vec{r}} C_\alpha(\vec{r})$$

and from equation (13) we get

$$\sum_{\alpha=1}^m v_\alpha \tilde{C}_\alpha(0) = V \quad (14)$$

and with the condition $q^3 V \gg 1$

$$\sum_{\alpha=1}^m v_\alpha \tilde{C}_\alpha(\vec{q}) = 0 \quad (15)$$

In a scattering experiment, the scattering Amplitude (9) is written for a multicomponent system as

$$A(\vec{q}) = \sum_{\alpha=1}^m \sum_{a \in \alpha}^{N_\alpha} \sum_{j \in a}^{n_\alpha} a_{ja} e^{i\vec{q}\cdot\vec{r}_{ja}} \quad (16)$$

where a_{ja} is the scattering length of the j^{th} monomer of a α molecule. Generally the mixture contains one solvent. We indicate this solvent by setting $\alpha = 1$; and with the assumption of equal volume between monomers and solvent molecules, the scattering intensity becomes

$$A(\vec{q}) = \sum_{\alpha=2}^m \sum_{a \in \alpha}^{N_\alpha} \sum_{j \in a}^{n_\alpha} a_{ja} e^{i\vec{q}\cdot\vec{r}_{ja}} + a_1 \tilde{C}_1(\vec{q})$$

Using condition i) (equation 15) we can write

$$A(\vec{q}) = \sum_{\alpha=2}^m \sum_{a \in \alpha}^{N_\alpha} \sum_{j \in a}^{n_\alpha} b_{ja}^{(1)} e^{i\vec{q}\cdot\vec{r}_{ja}} \quad (17)$$

where

$$b_{ja}^{(1)} = a_{ja} - v_\alpha \frac{a_1}{v_1} \quad (18)$$

is the contrast length with respect of solvent molecule, for the monomer j of the α molecule. It is noteworthy that this result is coherent with the constant volume assumption only if the volume v_1 of the solvent molecule is equal to the volume v_α of the monomer. The result (18) applies

to any mixture as long as assumption i) is fulfilled. For the polymeric system this contrast notion holds true for scattering vector value such that

$$q \ll l^{-1} \quad (19)$$

where l is the monomer length. In that case the scattering length of a monomer α is the sum of the coherent scattering length a_i of each atom i (see table I) of this monomer

$$a_\alpha = \sum_i a_i \quad (20)$$

For example the scattering length for the normal polystyrene monomer (C_8H_8) is $a_H = 2.32 \times 10^{-12}$ cm and for the deuterated one (C_8D_8) $a_D = 10.70 \times 10^{-12}$ cm. These values clearly show that the contrast length (18) can have very different values for normal and deuterated polymers.

3.c Exact model-Forward scattering calculation

We now consider an experiment in which the scattering is produced by $\alpha = 1, \dots, m$ elementary particles fluctuating in a sample holder at fixed pressure P . The radiation intercepts a fixed volume fraction V of the sample. The number N_α of particles in V is allowed to fluctuate. With this assumption a general formula for the forward scattering

$$\lim_{q \rightarrow 0} \sum (q)$$

was derived by J. des Cloizeaux and G. Jannink^[26].

$$\lim_{q \rightarrow 0} \sum (q) = \beta^{-1} \left\{ \langle a | N \rangle^2 \frac{\chi_T}{V} + \langle b' | G_E^{-1} | b' \rangle \right\} \quad (21)$$

In this expression $\beta = k_B T$, where k_B is the Boltzman constant and T the temperature. $\langle a |$ is the vector in the m dimensional space, $a = a_\alpha$ ($\alpha = 1, \dots, m$). a_α is the coherent scattering length (formula 20). $\langle N |$ is the vector N_1, \dots, N_m . χ_T is the isothermal compressibility of the system

$$\begin{aligned} \langle b' | &= |b\rangle - |t\rangle \frac{\langle t|b\rangle}{\langle t|t\rangle} \\ |b\rangle &= |a\rangle - |v\rangle \frac{\langle N|a\rangle}{\langle N|v\rangle} \end{aligned}$$

$|t\rangle$ is an arbitrary vector (but not perpendicular to $|n\rangle$). $|v\rangle$ is the vector v_1, \dots, v_m and G_E is the restriction of the operator

$$G_{\alpha\beta} = \left. \frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{\{N\}, P} \quad (22)$$

to the plane perpendicular to $|t\rangle$. $\left. \frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{P, \{N\}}$ is the partial derivative of the chemical potential μ_α [36] considered as a function of pressure and the number of particles.

With the choice $|t\rangle = 1, 0, 0, \dots, 0$ we get the result obtained a long time ago [25] (the solvent index is 1) :

$$\lim_{q \rightarrow 0} \Sigma(q) = \beta^{-1} \left\{ \left(\sum_\alpha a_\alpha N_\alpha \right)^2 \frac{\chi_T}{V} + \sum_{\alpha, \beta \neq 1} b'_\alpha b'_\beta \left(\frac{\partial \mu_\alpha}{\partial N_\beta} \right)^{-1}_{\{N\}, P} \right\} \quad (23)$$

where

$$b'_\alpha = a_\alpha - v_\alpha \sum_{\gamma=1}^m a_\gamma \frac{N_\gamma}{V} \quad (24)$$

According to formula (5) we notice that in this case

$$b'_\alpha = k_0^2 \frac{\pi}{2\pi} V \left. \frac{\partial n}{\partial N_\alpha} \right)_{\{N\}, P} \quad (25)$$

a well known result of light scattering.

The forward scattering cross section (23) is then the sum of two terms related to

- the scattering length a_α , for the term proportional to the compressibility.

- the contrast length b'_α (equation 24) for the term proportional to the derivative of the chemical potential at constant pressure.

The expression (23) can be used to determine the thermodynamic quantities of the scattering system : the compressibility, the osmotic pressure

and the partial volumes v_α .

3.d Values of contrast length

The monomer contrast length defined by equation (18) is used in all neutron scattering experiments. The contrast length b'_α (equation 24) is expressed as a sum of these elementary lengths. Using the expression of the concentration $c_\gamma = N_\gamma/V$ of the γ particles, equation (24) becomes

$$b'_\alpha = a_\alpha - v_\alpha \sum_{\gamma=1}^m a_\gamma c_\gamma$$

and with the condition of equation (13)

$$b'_\alpha = \sum_{\gamma \neq \alpha} c_\gamma v_\gamma \left(a_\alpha - v_\alpha \frac{a_\gamma}{v_\gamma} \right) \quad (26)$$

then, setting

$$b_{\alpha\gamma} = \sum_{\delta=1}^{m_\alpha} b_{\delta\alpha}^{(1)}$$

and returning to the more general case, equation (18) may be written as

$$b_{\alpha\gamma} = a_\alpha - v_\alpha \frac{a_\gamma}{v_\gamma} \quad (27)$$

then from equation (26) and (27)

$$b'_\alpha = \sum_{\gamma \neq \alpha} c_\gamma v_\gamma b_{\alpha\gamma} \quad (28)$$

It is recalled that v_α is the molecular volume and c_α the concentration of the scattering units. Molecular volumes are related to partial specific volume w_α by the relation

$$v_\alpha = \frac{w_\alpha M_\alpha}{v_A}$$

where M_α is the molecular weight and v_A the Avogadro number. The quantities w_α are determined by densitometric methods^[27,28]. For a given experiment, the components of the mixture must be chosen in order to give a contrast length (equation 27) as large as possible. This quantity is calculated by the following way.

Let us consider coherent scattering lengths per unit volume

$$A_{\alpha} = \frac{a_{\alpha}}{v_{\alpha}}$$

the contrast length per unit volume is then

$$B_{\alpha\beta} = \frac{b_{\alpha\beta}}{v_{\alpha}} = \frac{a_{\alpha}}{v_{\alpha}} - \frac{a_{\beta}}{v_{\beta}} = A_{\alpha} - A_{\beta} \quad (29)$$

The values of the molecular scattering length a_{α} , the scattering length per unit volume A_{α} and the incoherent scattering cross section are given in Table II for various solvents and polymers.

The value of the contrast length $B_{\alpha\beta}$ per unit volume for a given mixture is obtained by the difference between the corresponding scattering length A_{α} . This difference can be visualized by the diagram of Figure 1 [29]^a: the values of A_{α} are displayed on a same scale for solvent molecules and monomers. The contrast length $B_{\alpha\beta}$ (equation 29) for a given solvent β and a given polymer α is then directly estimated.

The main interest of the neutron scattering technique is underlined by the comparison with the light scattering technique. In this case the expression of the contrast length is somewhat different. It is proportional to a readily measurable quantity, the increment of the refractive index as noted in equation 24. If this quantity is expressed as function of the concentration (in g cm^{-3}), the elementary contrast length is written

$$b_{\alpha\beta} = \frac{k_0^2}{2\pi} n_0 \left. \frac{\partial n}{\partial c_{\alpha}} \right|_{\{c\}, P} \left(\frac{M_{\alpha}}{v_{\alpha}} \right)$$

where n_0 is the solvent index. Using values given in reference [30], the values of $B_{\alpha\beta}$ for some polymer solvent systems are given in Table III.

TABLE II

Values of the coherent scattering length, coherent scattering length per unit volume and incoherent scattering cross section for some solvents and polymers (see ref. 29)

1. <u>Solvents</u>		a (10^{-12} cm)	A (10^{+10} cm cm ⁻³)	σ_i (barn)
Carbon disulphide	CS ₂	1.23	1.23	0.01
Benzene	C ₆ H ₆	1.75	1.19	480
	C ₆ D ₆	7.99	5.45	13.2
Cyclohexane	C ₆ H ₁₂	- 0.498	- 0.278	960
	C ₆ H ₁₂	11.99	6.69	26.5
Toluene	C ₇ H ₈	1.66	0.94	640
	C ₇ D ₈	10	5.68	17.7
Water	H ₂ O	- 0.168	- 0.56	160
	D ₂ O	1.914	6.40	4.4
2. <u>Polymers</u>				
Ethylene	-CH ₂ -	- 0.08	- 0.31	160
	-CD ₂ -	2	7.44	4.4
isoprene	-C ₅ H ₈ -	0.33	0.27	640
	-C ₅ D ₈ -	8.67	5.12	17.6
Styrene	-C ₈ H ₈ -	2.32	1.41	640
	-C ₈ D ₈ -	10.7	6.61	17.6

TABLE III

Index increment, solvent index n_o [30] and contrast length per unit volume for a wavelength radiation $\lambda_o = 5460 \text{ \AA}$ for polystyrene solutions

Solutions	$\partial n / \partial c (\text{cm}^3 \text{g}^{-1})$	n_o	$B_{\alpha\beta} (10^8 \text{ cm cm}^{-3})$
Polystyrene/Benzene	0.1034	1.498	0.34
-Cyclohexane	0.1682	1.424	5.3
-Toluene	0.109	1.494	3.6
-CS2	~ 0	1.63	~ 0

Comparison with values obtained from figure 1, shows that the neutron contrast length is greater than these values by one or two order of magnitude. This result is obtained by using mixture of deuterated and hydrogenous molecules. This effect can be enhanced by the use of contrast variation allowed by the great difference in contrast length of labeled and unlabeled molecules. This variation is achieved by changing the composition of one or more species of the mixture. For example this can be done by a mixture of X deuterated and 1-X normal solvent molecules. Then the scattering length $a_1(x)$ of one solvent molecule (subscript 1) is

$$a_1(x) = x a_D + (1-x) a_H \quad (30)$$

where a_D and a_H are respectively the scattering length of the deuterated and hydrogenous molecule. The contrast length (equation 27) becomes

$$b_{a1}(x) = a_a - v_a \frac{a_1(x)}{v_1} \quad (31)$$

It is also possible to modify the scattering length of the solute by substitution of a fraction Y of deuterated molecules to the solute molecules.

By using the selective labeling and the contrast variation more informations can be obtained from a neutron scattering experiment than with other radiations. This point will be discussed in section 4.

3.e Experimental examples

Some examples of intensity scattered by polymer sample are given on figure 2,3 and 4.

Two curves are displayed on each figure. The upper one is the scattered intensity by the polymer mixture (polymer-solvent, polymer-polymer-solvent or polymer-polymer). It is the intensity given by equation (11). The lower one corresponds to the scattering by the "solvent" and is called the background. The excess scattering, obtained by subtraction of the two curves, contains all the information about the structure of the scattering medium, as given by equation (12).

- Figure 2 shows the scattered intensity for two solutions of deuterated polystyrene in carbon disulphide. The concentrations are respectively $0,005 \text{ g cm}^{-3}$ and $0,04 \text{ g cm}^{-3}$. In that case the background is the pure solvent CS_2 , and the contrast is maximum as indicated by Figure 1.

- The scattered intensity displayed on Figure 3 is recorded for a solution of hydrogeneous polystyrene in carbon disulphide. This solution contains a concentration $C_D = 0,005 \text{ g cm}^{-3}$ of deuterated polystyrene of same molecular weight. The total concentration is $C_T = 0,04 \text{ g cm}^{-3}$. In that case the background is a solution of protonated polystyrene with a concentration $C_T = 0,035 \text{ g cm}^{-3}$. The data displayed on this figure emphasize the great contrast difference between the two polymer samples (see Figure 1).

- Typical scattered intensities recorded for bulk samples are shown in figure 4. The upper curve corresponds to the scattering by deuterated polystyrene, dispersed in a matrix of undeuterated polystyrene. The concentration is $C_D = 0,01 \text{ g cm}^{-3}$. The lower curve corresponds to the scattering by undeuterated polystyrene bulk material. Ideally this curve should show no dependence on scattering vector. The increase at low angle is due to the divergence of the incident beam, since even without sample such an

effect is observed.

The two last examples are an application of equation (23) for incompressible mixtures :

i) First we consider the case where the number of component $m=2$. For a simple mixture with two components, where the solute concentration is c_2 , equation (23), modified by a standard thermodynamic derivation [31] becomes :

$$\lim_{q \rightarrow 0} \Sigma(q) = \beta^{-1} v b_2^2 c_2 \left(\frac{\partial \pi}{\partial c_2} \right)^{-1} \quad (32)$$

Then, measurements of the scattering cross section at the long wavelength limit lead to the determination of the osmotic compressibility $\chi_{T0} = \partial c_2 / \partial \pi$.

Precise determination of this quantity requests a so called "absolute" measurement. Up to now this raises technical difficulties in neutron-scattering experiments. These difficulties do not appear in light scattering experiments. Typical values are displayed on figure 5. Two set of data are shown, both recorded for polystyrene solution in the semi-dilute range : for the first one (open circle) the molecular weight is 7×10^6 and the solvent, benzene [32]. The second one is obtained from a solution in trans-Decalin at 40°C , the molecular weight being $1,3 \times 10^7$ [33]. These data are consistent with the scaling law prediction [7] :

$$\chi_{T0} \sim c^{-5/4}$$

as displayed by the line with the slope $1/4$.

ii) When the number m of components is greater than two, the relation between $\Sigma(q)$ and thermodynamic quantities is less straightforward. When $m = 2$, relation (23) leads to the determination of the unique unknown term. For $m > 2$ we need some supplementary relations. They can be obtained by varying the contrast lengths b_α . This method can be applied to cases where there are mutual interactions between components, described by chemical affinities. This is the case of polyelectrolyte solutions in water with added salt. If the water is denoted by 1, the salt by 2 and the polyelectrolyte by 3, the scattering cross section is then written as [37]

$$\lim_{q \rightarrow 0} \Sigma(q) = \beta^{-1} \left\{ \frac{N_3}{V} \frac{(b_3 + \zeta b_2)^2}{1 - (N_3/V)(v_3 + \zeta v_2)} \left(\frac{\partial \pi}{\partial N_3 D} \right)^{-1} + \frac{v_3^2}{G_{22}} \right\} \quad (33)$$

The index D indicates that the Osmotic pressure gradient is to be measured at the dialysis equilibrium. The coefficient ζ is

$$\zeta = - G_{23} / G_{22}$$

It is related to the preferential interaction coefficient between the salt and the polyelectrolyte [34]. The quantities $G_{\alpha\beta}$ are given by equation (22). Relation (33) has been extensively used in light scattering experiment. Neutron scattering technique leads to a more complete information, because the contrast length can be varied. Following the equations (28) and (30) we get

$$b_q(x) = a_d - v_d \left\{ (x a_D + (1-x) a_H) c_1 + a_2 c_2 + a_3 c_3 \right\}$$

where a_H and a_D are the scattering length for protonated and deuterated solvent. Let us suppose that there is a fraction x_1 for which $b_2(x_1) = 0$. In that case the scattering cross section (33) is only proportional to the osmotic pressure gradient. This quantity does not depend on the solvent composition x .

If there exists another solvent composition x_0 such as

$$b_3(x_0) + \zeta b_2(x_0) = 0 \quad (34)$$

This expression gives a direct means to determine the preferential interaction coefficient as long as the second term of the right hand of equation (33) can be treated as a background. Experimental test of equation (34) has been done with solution of deuterated sulfonated polystyrene in a mixture of light and heavy water, with and without added salt [35]. The results are reported on figure 6. The square root of the recorded intensity at very small q value is plotted versus the content of light water. The value of the coefficient ζ is calculated from equation (34). It can be seen that the value x_0 of the volume fraction of D_2O in water for which equation (34) holds true is a function of the added salt. Value of x_0 for a solution without salt has been determined previously [48].

4. THE SCATTERING FUNCTION

4.a The form factor and the structure factor

For an incompressible solution of N polymers in a solvent, the coherent elastic cross section (equation 10) is written as

$$\Sigma(q) = \left\langle \sum_{\alpha\beta} \sum_{ij} b_{i\alpha} b_{j\beta} e^{i\vec{q} \cdot (\vec{r}_{i\alpha} - \vec{r}_{j\beta})} \right\rangle \quad (35)$$

i and j being the indices of monomers belonging to polymers α and β respectively. $r_{i\alpha}$ and $b_{i\alpha}$ are the positions and contrast length (relation 18) of the ith monomer in molecule α . The sum in relation (35) can be splitted in two terms. If, for reasons of simplicity, let us assume that the polymers are identical in all respects ($b_{i\alpha} \equiv b$), including molecular weight, we get

$$\frac{\Sigma(q)}{b^2} = \left\langle \sum_{\alpha=\beta} \sum_{ji} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle + \left\langle \sum_{\alpha, \beta \neq \alpha} \sum_{ij} e^{i\vec{q} \cdot (\vec{r}_{i\alpha} - \vec{r}_{j\beta})} \right\rangle$$

which can be written

$$\frac{\Sigma(q)}{b^2} = N S_1(q) + N(N-1) S_2(q) \quad (36)$$

where $S_1(q)$ is the polymer form factor which describes the conformation of one chain, and $S_2(q)$ is the structure factor of the solution.

$$S_1(q) = \left\langle \left| \sum_{j \in \alpha} e^{i\vec{q} \cdot \vec{r}_{j\alpha}} \right|^2 \right\rangle$$

$$S_2(q) = \left\langle \sum_{\substack{j,k \\ \alpha, \beta \neq \alpha}} e^{i\vec{q} \cdot (\vec{r}_{j\alpha} - \vec{r}_{k\beta})} \right\rangle$$

These two terms describe the mean configuration of polymers in solution and are function of the concentration. The main problem in a scattering experiment is the determination of these two unknown functions. This can be achieved by the following ways :

i) usually the determination of the first term is done by measuring the coherent scattering cross section for different concentrations. The extrapolation to the zero concentration limit gives the form factor $S_1(q,0)$. This method can be used in all scattering experiments but in neutron scattering it is more easy to chose a good contrast between polymer and solvent.

ii) the second method use the selective labeling of the polymer. The solution is a mixture of labeled and normal polymers. The total concentration being fixed, the extrapolation is now done on the labeled molecules concentration. This gives the form factor $S_1(q,c)$ at a given concentration c . This method has been used in some X-ray scattering experiment [38], but is more powerful in neutron scattering.

iii) a more useful way leads to the determination of the two terms for any concentration. This way use the selective labeling and the contrast variation.

The use of this last method generalize the two others, so we will describe it in details [8].

Let X the number fraction of labeled molecule solvent with coherent scattering length a_{L1} . The scattering length of a solvent molecule is according relation (30)

$$a_1(x) = x a_{L1} + (1-x) a_1$$

and the contrast length of a monomer is then

$$b_1(x) = a - v \frac{a_1(x)}{v_1(x)} \quad (37)$$

where

$$v_1(x) = x v_1 + (1-x) v_{L1}$$

a is the scattering length and v the molecular volume of the monomer, v_1 and v_{L1} the molecular volume of the normal and deuterated solvent molecule.

If the solution contains a number fraction Y of labeled polymer mole-

cules, the contrast length of a labeled monomer with coherent scattering length a_L and molecular volume v_L is

$$b_{L1}(z) = a_L - v_L a_1(z) / v_1(z) \quad (38)$$

Returning to the general case, a straightforward calculation reduces the coherent scattering (relation 35) to

$$\Sigma(q, c, x, y) = N \langle b^2(y) \rangle S_1(q, c) + N(N-1) \langle b(y) \rangle^2 S_2(q, c) \quad (39)$$

where

$$\left. \begin{aligned} \langle b(y) \rangle &= b_1(x) + \gamma (b_{L1}(x) - b_1(x)) \\ \text{and} \\ \langle b^2(y) \rangle &= b_1^2(x) + \gamma (b_{L1}^2(x) - b_1^2(x)) \end{aligned} \right\} \quad (40)$$

Relation (39) provides the way to determine the two unknown quantities $S_1(q, c)$ and $S_2(q, c)$, by doing two experiments with two different contrast lengths. This fact will be discussed in details below.

If we use the total scattering function $S_T(q, c)$ defined as

$$S_T(q, c) = N S_1(q, c) + N(N-1) S_2(q, c)$$

the relation (39) can be written as [39]

$$\Sigma(q, c, x, y) = N\gamma(1-\gamma) (b_{L1}(x) - b_1(x))^2 S_1(q, c) + \langle b(y) \rangle^2 S_T(q, c) \quad (41)$$

we can now discuss how the unknown functions $S_1(q, c)$ and $S_2(q, c)$ can be extracted from relation (39) or (41). There are three experimental situations :

1 - Solution of identical labeled polymers. In that case $\gamma = 1$ and

relation (41) reduces to

$$\Sigma(q, c, x, 1) = b_{L1}^2(x) S_T(q, c) \quad (42)$$

the experiment yields a measure of the correlation between all monomers. The contrast variation is not generally used.

2 - In the bulk, the system is assumed to be incompressible. The total scattering functions $S_T(q)$ should vanish, as recently experimentally verified [40]. The scattering experiment provides a measurement of the single chain form factor $S_1(q, c_B)$, where c_B is the bulk concentration

$$\Sigma(q, c_B, Y) = N Y(1-Y) (a_L - a)^2 S_1(q, c_B) \quad (43)$$

Furthermore this expression indicates that $S_1(q, 1)$ can be obtained even with a high concentration of labeled polymer, as already emphasized in earlier experiment on bulk polystyrene [10]. The scattered intensity will reach the maximum for $Y = 1/2$.

3 - We can now discuss the use of the contrast variation defined by relation (30). Let us suppose that there is a number fraction x_0 of deuterated solvent molecule such that

$$b_1(x_0) = 0 \quad (44)$$

then relation (39) take the simple form

$$\Sigma(q, c, x_0, Y) = N b_{L1}^2(x_0) Y S_1(q, c) + N(N-1) b_{L1}^2(x_0) Y^2 S_2(q, c) \quad (45)$$

now if we took another number fraction Y of deuterated polymer, for example $Y = 1$, we get

$$\Sigma(q, c, x_0, 1) = N b_{L1}^2(x_0) S_1(q, c) + N(N-1) b_{L1}^2(x_0) S_2(q, c) \quad (46)$$

By combining these two equations with two unknown quantities it is possible to determine the form factor $S_1(q, c)$ and the structure factor $S_2(q, c)$

with only two experiments :

$$N b_{11}^2(x) \gamma(1-\gamma) S_1(q, c) = \sum (q, c, x_0, \gamma) - \gamma^2 \sum (q, c, x_0, 1) \quad (47)$$

and

$$N(N-1) b_{11}^2(x) \gamma(1-\gamma) S_2(q, c) = \sum (q, c, x_0, \gamma) - \gamma \sum (q, c, x_0, 1) \quad (48)$$

This method is based on the fact that the relation (44) is fulfilled. Values given on figure 1 indicates that this fraction x_0 exists in nearly all practical cases. For example, $x_0 = 0.10$ for normal polystyrene in toluene and $x_0 = 0.25$ for normal polystyrene in cyclohexane. If it is not possible to fulfil equation (44), relation (39) can be used in exactly the same way as relation (45).

4.b Scattering vector ranges and physical information.

The scattered intensity is seen to depend considerably upon the scattering vector q and this dependence is due to the existence of typical correlation ranges :

- In the "Guinier range" (relation 7) the form factor $S_1(q, c)$ is expressed as [26]

$$S_1(q, c) = 1 - \frac{q^2 R_g^2}{3} \quad (49)$$

thus providing a measure of the radius of gyration.

- In the intermediate range (relation 8) the detail of the polymer conformation is observed. In this range the scattering function is described by a power law of the scattering vector. For flexible polymer coil in dilute solution, the form factor can be written as [6]

$$S_1(q, c \rightarrow 0) \sim q^{-4/\nu} \quad (50)$$

where ν is the excluded volume exponent. In semi-dilute solutions the

scattering function is expressed by a Lorentzian form^[11]

$$S_T(q, c) \sim \frac{1}{q^2 + \xi(c)^{-2}}$$

from which the value of the screening length can be determined.

4.c Experimental examples

In order to give an illustration of SANS we have selected the example of the determination of the polymer conformation in the bulk and in semi dilute solutions. This study needs measurements of the form factor $S_1(q, c)$ which has been extracted from the scattering cross section by methods described in section 4a i) and 4a ii).

i) Bulk polymer . Experiments have been carried out in the Guinier range (equation 7) with samples of bulk amorphous polystyrene. These samples were a mixture of protonated polystyrene containing deuterated polystyrene with concentration ranging from 0.5 to $2 \times 10^{-2} \text{ g cm}^{-3}$. Different samples were made with different molecular weight M_w .

A typical example of the intensity scattered by such a sample is shown in figure (4). The determination of the form factor $S_1(q, 0)$ is carried out by the method described in section 4a i) and the value of the radius of gyration is obtained by using relation (49). The result is displayed in figure 7.

It was found that the coil configuration behaves in a way similar to the random walk, i.e.

$$R_G \sim M_w^{0.5}$$

This relation was predicted^[12] a long time ago but could only recently be tested when neutron scattering was made available.

The same relationship holds true for the polymer coil in a poor solvent, i.e. a solution at a temperature close to the critical demixtion temperature T_c . The polymer coil in a good solvent (i.e. in a solution at a temperature far away from T_c), exhibits a different behaviour. It is namely found that

$$R_G \sim M_w^{\nu}$$

where $\nu \approx .6$. the comparison between these three situations clearly support the theoretical prediction : the polymer conformation is the same in poor solvent and in the bulk.

This can also be proved by studying the scattering vector dependence of the scattering law in the intermediate range (equation 8), for three dilute solutions : in good solvent, in poor solvent, and in the bulk. The plot of the inverse of the scattered intensity as a function of q is shown in figure 8 in a log-log scale. According to relation (50) this is another way to determine the value of the excluded volume exponent. Again the value of ν obtained in the bulk indicates the absence of an effective excluded volume interaction.

ii) Concentration effects. These results obtained in the bulk state raise the question of the polymer configuration variation with the concentration. The situation was clear in the two extreme concentrations : for dilute concentration the polymer chain is expanded, and the exponent in the power law dependence of the radius of gyration on the molecular weight is 0.6 (see figure 7). At the bulk limit this exponent is 0.5.

Classical theory [12] predicted a decrease of the polymer dimension up to the overlap concentration C^* (At that concentration the polymer chains begin to interpenetrate each other), where the polymer chain is in unperturbed state. In the scaling law description [7] the radius of gyration behaves as $C^{-0.25}$ for $C > C^*$.

This concentration dependence was tested in the following scattering experiment. The samples were a mixture of deuterated and protonated polystyrene dissolved in a good solvent. The form factor $S_1(q,c)$ is obtained by using the extrapolation described in section 4a ii). An example of such an extrapolation is displayed on figure 9 for three total concentrations. The values of R_G as a function of the concentration are given in figure 10 with a log-log scale. The variation is in agreement with the prediction of the scaling law theory. This variation expresses the fact that when the concentration increases, the intramolecular interactions become screened due to intermolecular interactions between segments on different chains. This effect is described by the screening length ξ [16]. For distances larger than ξ the portions of the same polymer chain have "forgotten" the presence of segments inside the length ξ , hence leading to an absence of excluded volume interaction. Within the length ξ excluded volume still plays a role. This length varies with the concentration according the relation [7];

$$\xi \sim C^{-3/4}$$

This length can be measured in a scattering experiment with a semi-dilute solution of identical polymers. According to relation 42 this experiment leads to the determination of the total scattering function $S_T(q,c)$. In that case this function is given by relation (51). A typical example of the intensity scattered by such a sample is given on figure 2. The inverse of the scattering cross section is plotted on figure 11 in function of the square of the scattering vector. The lower curve corresponds to data recorded for dilute solution, and the variation is given by relation (50) where $\nu = 0.6$.

The values of ξ , given by the abscisse intercept in figure 11, are displayed on figure 12 as a function of concentration in a log-log scale. The value of the slope (0.72) is in good agreement with theoretical predictions.

The above examples are an illustration of what the use of neutron scattering has brought in the field of polymer physics. Since these first experiments many other studies of the influence of temperature or concentration on polymer conformation have been done. It is not possible to give an exhaustive review of all these works^[50]. They concern amorphous polymers^{[[41] to [44]]}, gels and networks^[45] and crystalline polymers^{[46][47]}.

As pointed out recently^{[48][49]}, the use of the method described in section 4a iii) allows the measurement of the form factor $S_1(q,c)$:

i) Equation 45 provides a useful graphical method giving $S_1(q,c)$ and $S_2(q,c)$ from a plot of $\Sigma(q,c,x_0,y)/y$ versus $y+q$. This method has been applied^[51] to data recorded in the experiment described in section 4c i). The result is displayed on figure 13 for two total concentrations, one ($c_T = 0,1 \text{ g cm}^{-3}$) above and the other ($c_T = 0.03 \text{ g cm}^{-3}$) below the overlap concentration c^* . The extrapolation to zero concentration in labeled polymer gives the form factor $S_1(q,c)$. The structure factor $S_2(q,c)$ is obtained from the slope of these extrapolation lines. The data for the higher concentration show clearly the weakness of the interaction.

ii) This method is of particular interest when the q variation of the scattering cross section present a maximum. It is the case for scattered intensity by polyelectrolyte solution in pure water. A typical intensity distribution is shown in figure 14 for different polymer concentration^[52].

The form factor $S_1(q,c)$ and the structure factor $S_2(q,c)$ have been extracted using procedure described in section 4a iii). The result is displayed in figure 15. It shows that the broad peak appears exclusively in $S_2(q,c)$ and consequently is due to an intrachain interaction. Furthermore the negative sign corresponds to a repulsive interaction. This result is obtained in the intermediate scattering vector range (relation 12). The same treatment can be applied to data recorded in the Guinier range (relation 7) allowing the determination of the radius of gyration^[48].

iii) The last example is an illustration of equation 43. Data recorded for bulk polystyrene samples with increasing concentration of deuterated polymer of same molecular weight, are displayed on figure 16. The inverse of the scattered intensity multiplied by the factor $Y(1-Y)$ is plotted versus the square of the scattering vector. It shows that the form factor $S_1(q,c_B)$ can be determined even for high concentration of labeled polymers^[40].

This method will be applied for the study of polymers chain out of equilibrium, in the stretched state for example. The large amount of deuterated chains will compensate the low scattered intensity.

4.d New trends

SANS is a technique used to determine static correlation functions, characteristic of the sample structure.

Recently it has become of interest to derive static correlation functions from quasi elastic scattering. The functions obtained from the interpretation of such experiments are not weighted in the same manner as those obtained from SANS.

The comparison between elastic and quasi elastic scattering yields therefore valuable information on cross over problems^{[54][55]}. Results depend here on the performance of the spectrometer.

Let us now mention the application of SANS to the study of phenomena far from equilibrium (such as stress relaxation in rubbers). In this problem the experimental technique should be entirely reexamined. Use of spallation source could be of same advantage^[56].

A last remark concerns the study of homogeneous systems : the SANS technique associated with a high content of labelled material, promises many new results in the near future.

5. CONCLUSION

These last ten years the SANS technique has proved to be a powerful tool in polymer physics, turning to account two special features of this radiation : First the wavelength range which allows to bridge the gap existing in the scattering vector between light scattering and small angle X-ray scattering. (But in this last case the use of the new synchrotron radiation brings the same advantage). Experiments in the intermediate scattering vector range are easier than in light scattering and classical X-ray scattering, leading to more detailed informations about the local interactions between monomers at a scale of some ten Angströms to hundred Angströms.

Secondly the nature of the neutron-matter interaction gives a totally new insight in the field of polymer mixtures. This results in the expression of a contrast length described in section 3. A new derivation of this quantity extends this notion down to the limit of zero scattering vector range^[26]. With neutrons, this contrast length may be greater by one or two order of magnitude than the corresponding length for electromagnetic radiations. This is obtained by using a mixture of deuterated and hydrogenous molecules. The fact that isotopic labeling gives no important chemical perturbation (at least for amorphous polymers), allows the use of the contrast variation :

The contrast length of a polymer molecule can be varied by changing the amount of deuterated and hydrogenous molecules of the solvent.

The aim of a small angle scattering experiment by polymer solution is the determination of the polymer form factor S_1 and the structure factor S_2 . This was obtained in light scattering and X-ray scattering by a double extrapolation to zero scattering angle and zero concentration. The results are valid only at these limits. In the neutron scattering technique the two unknown functions S_1 and S_2 can be determined at any concentration by using the contrast variation method and the selective labeling of the polymer as described in section 4.

Up to now neutron scattering has been successfully used to check the predictions of the scaling law theory [7] for amorphous polymers. This was done by measuring the exponent of the power law dependence of molecular parameters, for example the radius of gyration and the screening length ξ . More precise results will be obtained by the use of "absolute" intensity measurements, together with the method described in section 4. New problems are now studied, such as the structure of polyelectrolyte solutions, partially labeled chains and stretched polymer.

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FIGURE CAPTIONS

Figure 1 : Scattering length by unit molecular volume for different solvents and polymers. The contrast length for a polymer-solvent mixture is given by the difference between these scattering lengths. (from reference 29).

Figure 2 : Scattered intensity as a function of the scattering vector q for solutions of deuterated polystyrene ($M_w = 5 \times 10^5$) in good solvent (CS_2) for two concentrations. The scattered intensity by pure solvent (closed circles) has been multiplied by a factor 2.

Figure 3 : Plot of the scattered intensity versus scattering vector for a solution of protonated polystyrene ($M_w = 5 \times 10^5$) in a good solvent (CS_2). This solution contains a concentration of $C_D = 0.005 \text{ g cm}^{-3}$ of deuterated polystyrene ($M_w = 5 \times 10^5$). The total concentration is $C_T = 0.04 \text{ g cm}^{-3}$. The lower curve is the intensity scattered by a solution of protonated polystyrene ($C_H = 0.035 \text{ g cm}^{-3}$).

Figure 4 : Scattered intensity as a function of the scattering vector for bulk polystyrene with a concentration of $C_D = 0.01 \text{ g cm}^{-3}$ of deuterated polystyrene ($M_w = 2.1 \times 10^4$). The lower curve is the intensity scattered by the protonated matrix ($M_w = 2 \times 10^4$). (figure 5 of reference 10).

Figure 5 : Log-log representation of the osmotic compressibility χ (multiplied by concentration C) versus concentration for polystyrene solutions.

- open circles - molecular weight $M_w = 7 \times 10^6$, solution in benzene (data taken from reference 32).
 - closed circles - molecular weight $M_w = 1,3 \times 10^7$, solution in trans-Decalin at 40°C . (Data taken from reference 33).
- The line with slope $1/4$ corresponds to the scaling law prediction.

Figure 6 : Variation of the square root of the scattered intensity at low scattering vector, as a function of the composition X of the mixture light water - heavy water, for a solution of polyelectrolyte (sulfonated polystyrene $M_w = 3 \times 10^4$), with ($C_S \neq 0$) and without salt ($C_S = 0$). Polymer concentration $C_p = 4.76 \times 10^{-2} \text{ g cm}^{-3}$. Concentration of added salt (NaBr) $C_S = 1.47 \times 10^{-3} \text{ g cm}^{-3}$. The value X_0 of the volume fraction $1 - X$ of D_2O in water for which equation 34 holds true is a function of added salt [35].

Figure 7 : Radius of gyration plotted versus molecular weight in a log-log scale. The experimental data are obtained in different environments : \emptyset in the bulk, $+$ in a theta solvent (cyclohexane), X in a good solvent (CS_2). (reproduction of figure 8 of reference 10).

Figure 8 : Inverse of the scattered intensity plotted versus scattering vector in a log-log scale for polymer in three dilute solutions :
A - solution of deuterated polystyrene ($M_w = 1.2 \times 10^6$) in good solvent (CS_2) - concentration $C = 2.5 \times 10^{-3} \text{ g cm}^{-3}$.
B - solution of protonated polystyrene ($M_w = 3.8 \times 10^6$) in theta solvent (deuterated cyclohexane, theta temperature $40^\circ C$) - concentration $C = 5 \times 10^{-3} \text{ g cm}^{-3}$.
C - solution of deuterated polystyrene ($M_w = 1.1 \times 10^6$) in a matrix of hydrogenous polystyrene of same molecular weight. Concentration $C = 2.05 \times 10^{-2} \text{ g cm}^{-3}$.
(reproduction of figure 1 of reference 6).

Figure 9 : Inverse of the intensity scattered by solutions of hydrogenous polystyrene ($M_w = 1.14 \times 10^5$) containing few deuterated polystyrene (same molecular weight), as a function of the square of the scattering vector (here noted r^2). C_D is the concentration of labeled polymer ($C_D = 0.02 ; 0.015 ; 0.01$ and 0.005 g cm^{-3}). C is the total concentration $C = C_D + C_H$. Extrapolation to $C_D = 0$ gives the form factor $S_1(q, c \rightarrow 0)$. (reproduction of figure 5 of reference 11).

Figure 10 : Log-log plot of the square of the radius of gyration divided by the molecular weights as a function of the concentration. Data are obtained for two different molecular weights : closed circles $M_w = 1.4 \times 10^5$, open triangles $M_w = 5 \times 10^5$. The slope determined by this plot is in excellent agreement with the scaling law prediction (reproduction of figure 7) of reference 11).

Figure 11 : Inverse of the scattered intensity as a function of the square of the scattering vector q . Samples are solutions of deuterated polystyrene in good solvent (CS_2) at two concentrations.
- upper curve $M_w = 5 \times 10^5$, $C = 0.15 \text{ g cm}^{-3}$ (semi dilute range)
- lower curve $M_w = 1.1 \times 10^6$, $C = 0.001 \text{ g cm}^{-3}$ (dilute range)
Note the difference in behavior. Value of the screening length is given by the extrapolation of the semi dilute solution curve.

Figure 12 : Log-log plot of the screening length ξ as a function of concentration. The screening length is determined from the Lorentzian broadening (equation 51) of the scattered curves measured in the semi dilute range. Data are recorded for three different molecular weights :
closed circles $M_w = 2.1 \times 10^6$; closed triangles $M_w = 6.5 \times 10^5$;
open circles $M_w = 5 \times 10^5$. (reproduction of figure 12 of reference 11).

Figure 13 : Determination of the form factor $S_1(q,c)$ and the structure factor $S_2(q,c)$ by using equation 45 : Samples are a mixture of deuterated and hydrogenous polystyrene in solution in good solvent. The data are the same as in figure 9.

Figure 14 : Scattered intensity as a function of the scattering vector for a solution of deuterated sulfonated polystyrene in pure water for different concentrations (in g cm^{-3})

$\cdot 10^{-2}$
+ 1.96×10^{-2}
o 4.76×10^{-2}
 $\Delta 9.09 \times 10^{-2}$
□ 13.04×10^{-2}
 $\blacktriangle 23 \times 10^{-2}$

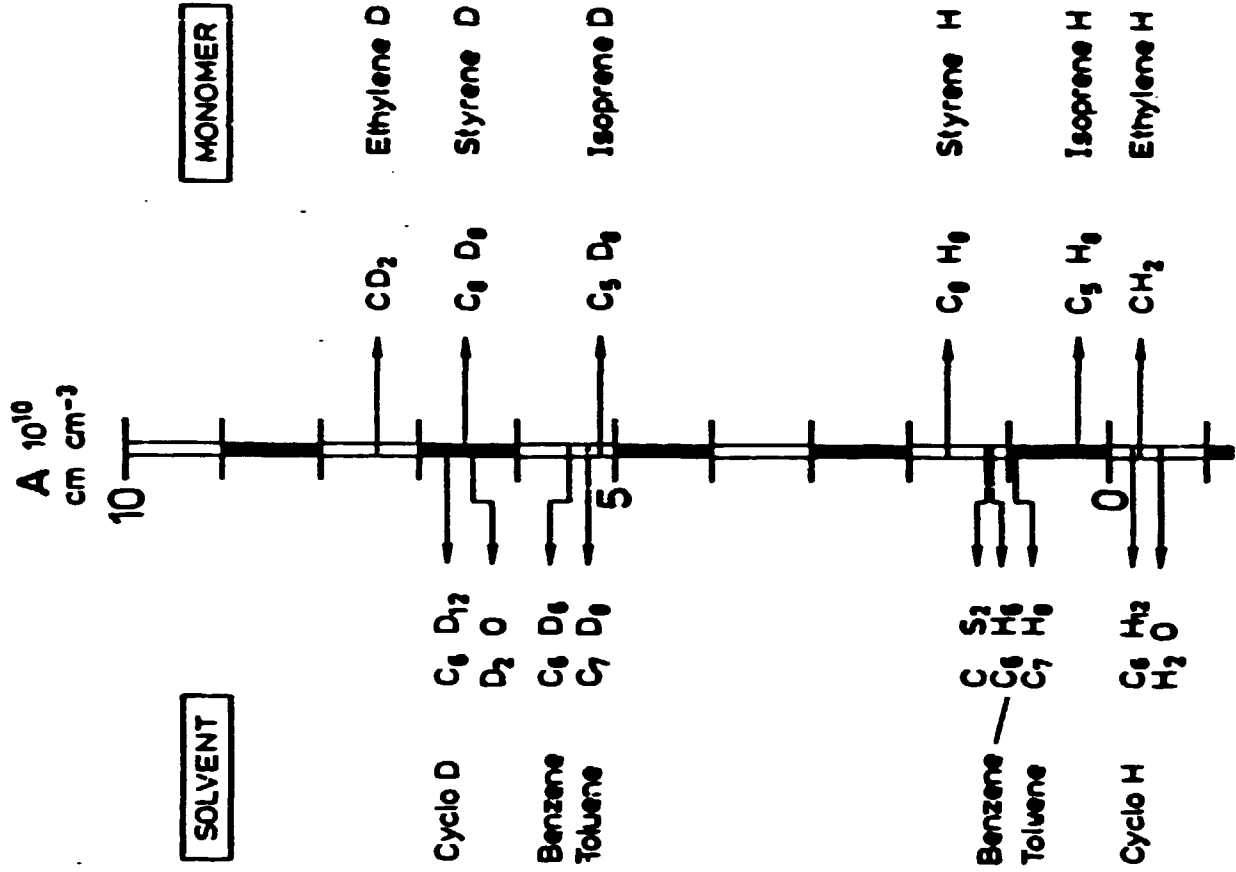
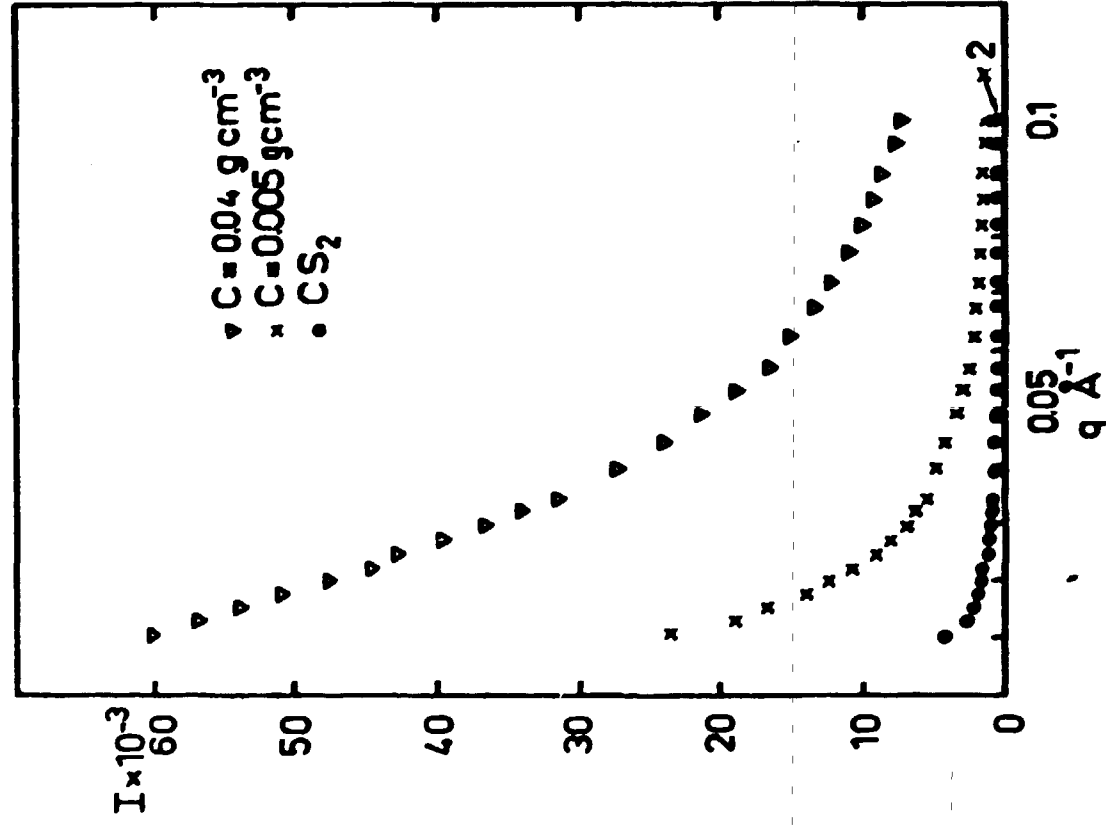
(reproduction of figure 3 of reference 52).

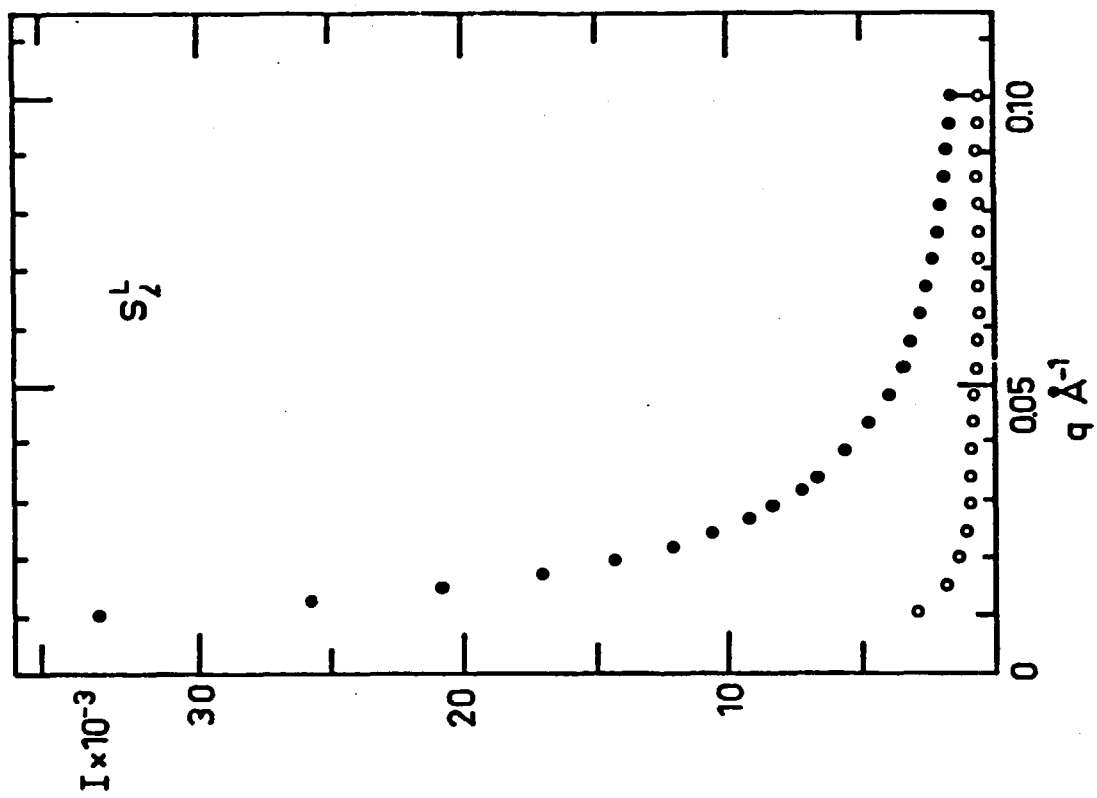
Figure 15 : Decomposition of the measured scattering function (curve b) in form factor (curve a) and structure factor (curve c). Data are recorded for a solution of sulfonated polystyrene ($M_w = 3 \times 10^4$) in solution in pure water ($C = 2 \times 10^{-2} \text{ g cm}^{-3}$). (figure 1 of reference 48).

Figure 16 : Inverse of the scattered intensity multiplied by $\varphi(1-\varphi)$ (φ the number fraction of labeled polymer) plotted versus the square of the scattering vector, for bulk protorated polystyrene ($M_w = 6.7 \times 10^5$) with increasing content of deuterated polymer ($M_w = 6.2 \times 10^5$). All these curves are nearly identical showing that the form factor can be obtained from equation 43.

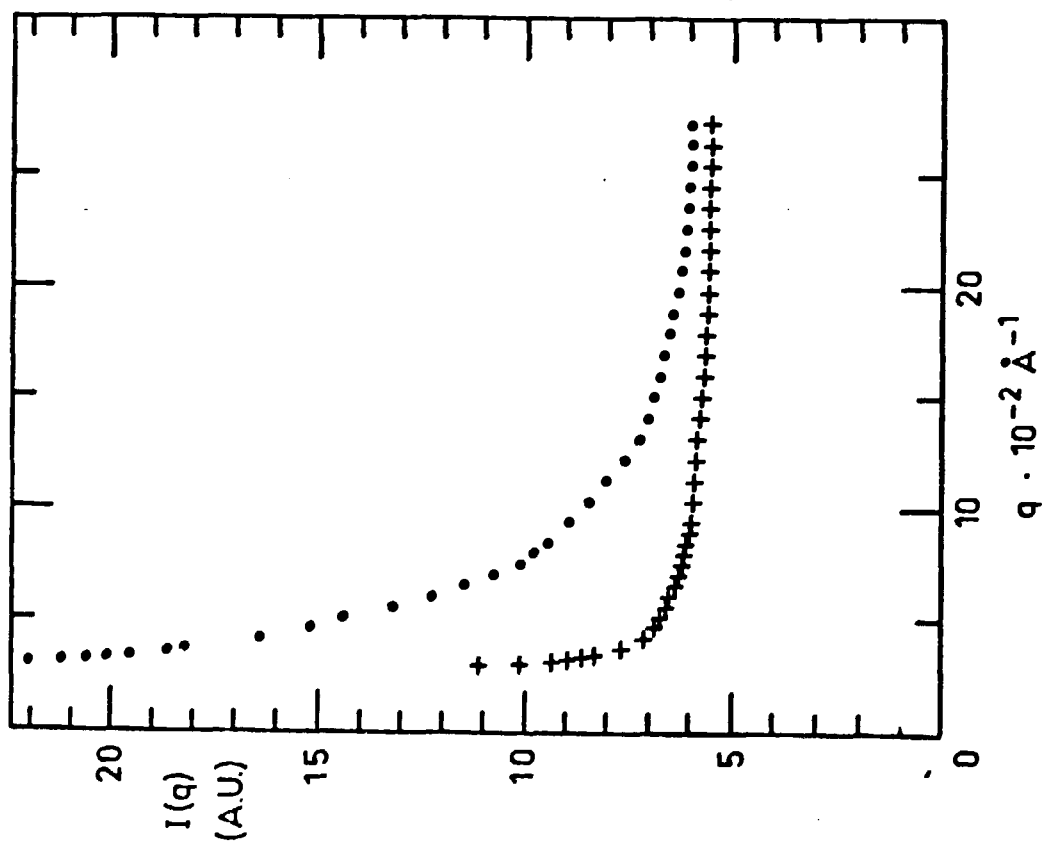
Units of symbol

a	coherent scattering amplitude
N_A	Avogadro number
$A(q)$	scattering amplitude
A	coherent scattering length per unit volume
b	contrast length
B	contrast length per unit volume
C	concentration of elementary scatterers
$I(q)$	scattered intensity
K	contrast factor
\vec{k}_0	incident wave vector
\vec{k}	scattered wave vector
l	monomer length
m_n	neutron mass
M	molecular weight
n	refractive index
N	number of scatterers
\vec{q}	scattering vector
R_G	radius of gyration
$S(q)$	scattering function
$S_1(q)$	form factor
$S_2(q)$	structure factor
v	scattering volume of the elementary scatterer
V	scattering volume
w	partial specific volume
Z	effective number of scattering electrons
α	polarizability
λ	wavelength
v	excluded volume exponent
θ	scattering angle
χ_T	isothermal compressibility
ξ	screening length

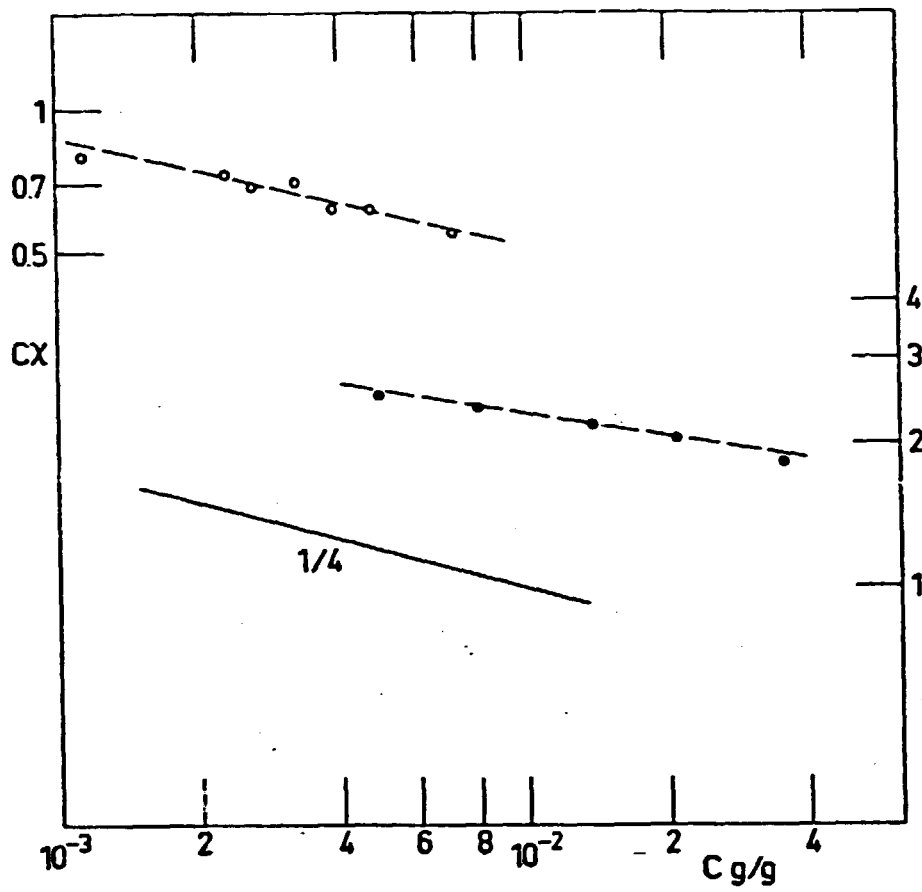




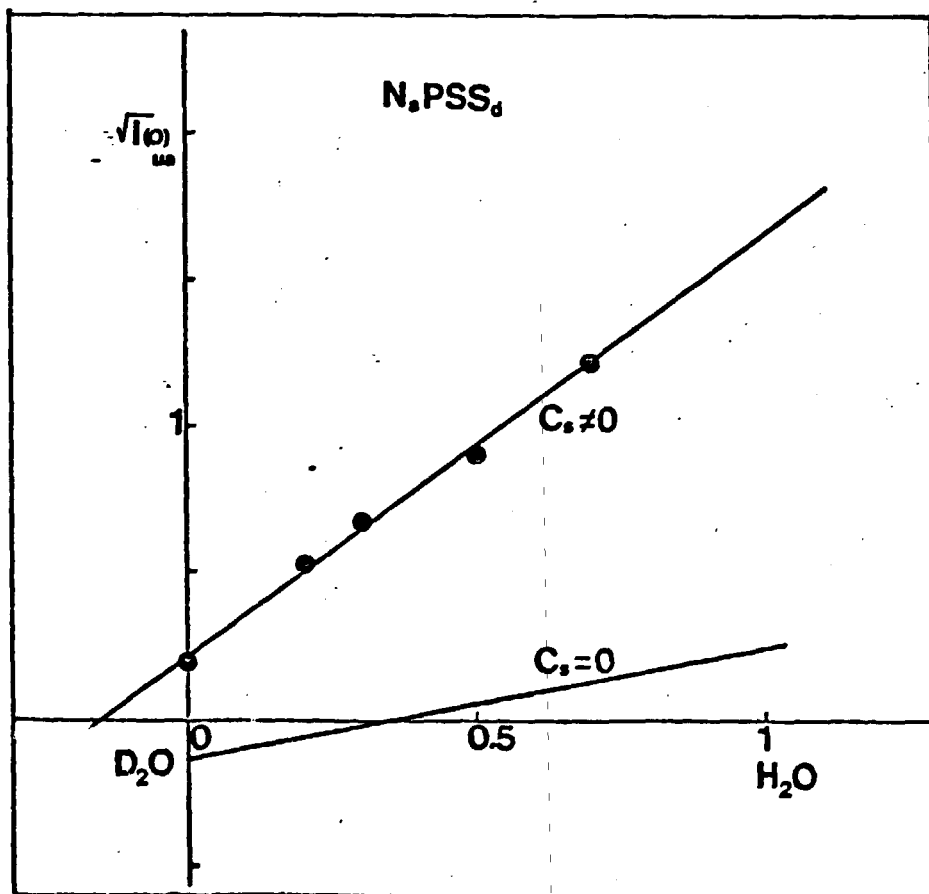
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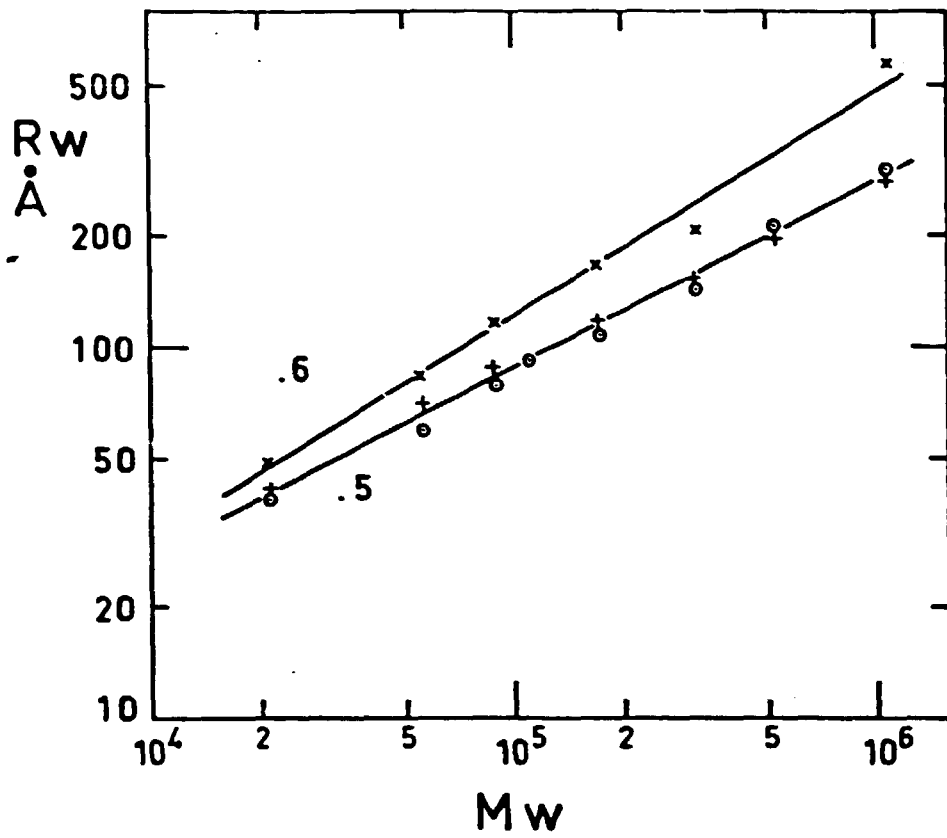


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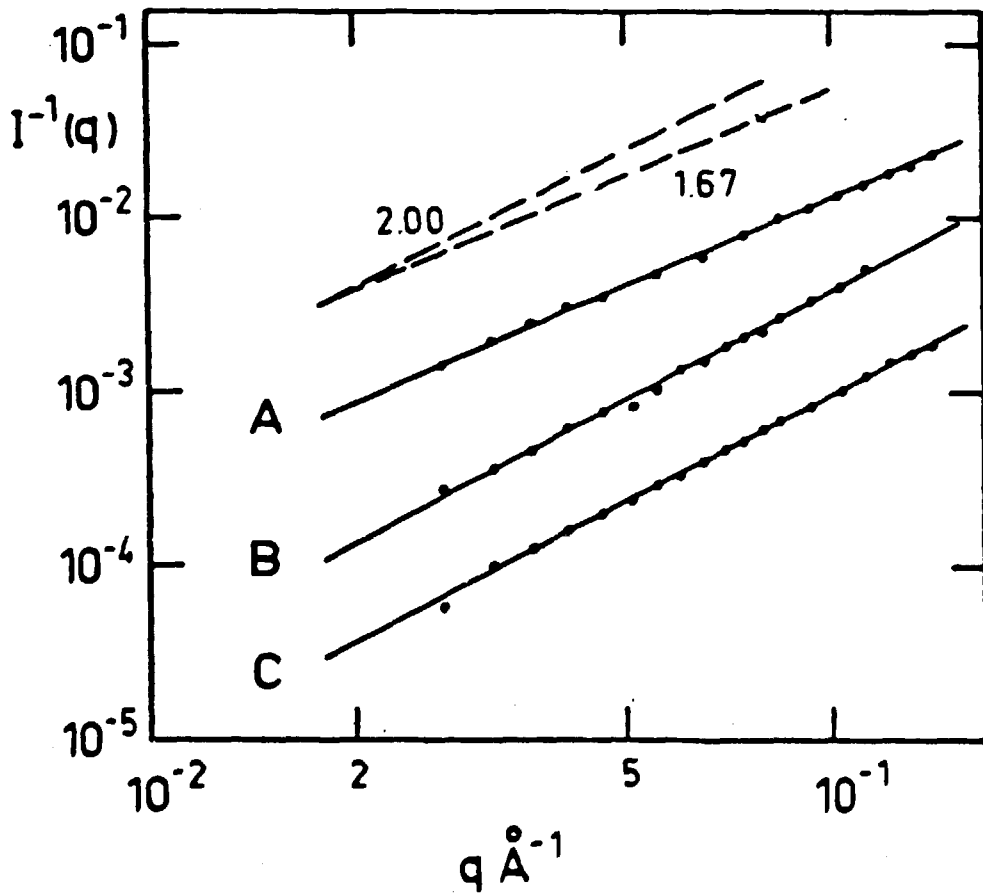


$$C_p = 4,76 \cdot 10^{-2} \text{ gcm}^{-3}$$

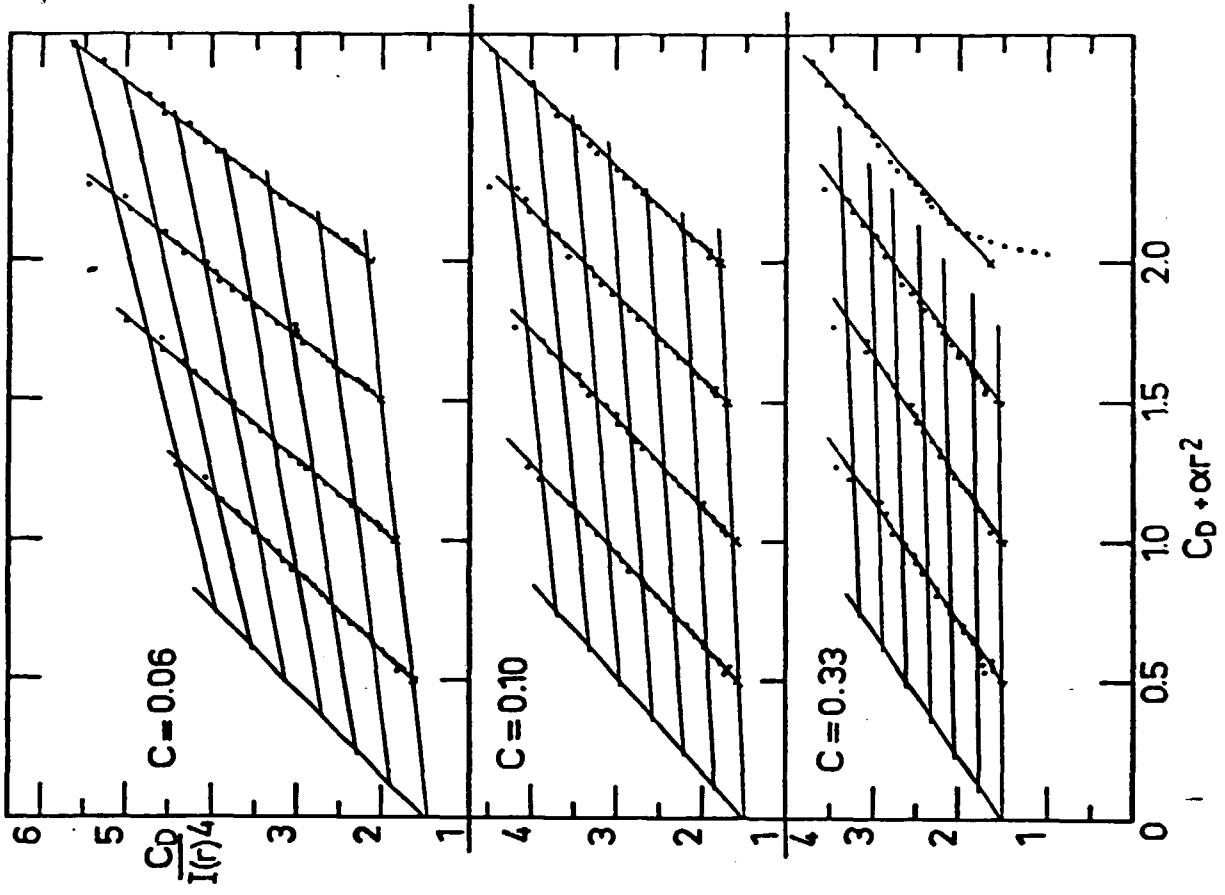
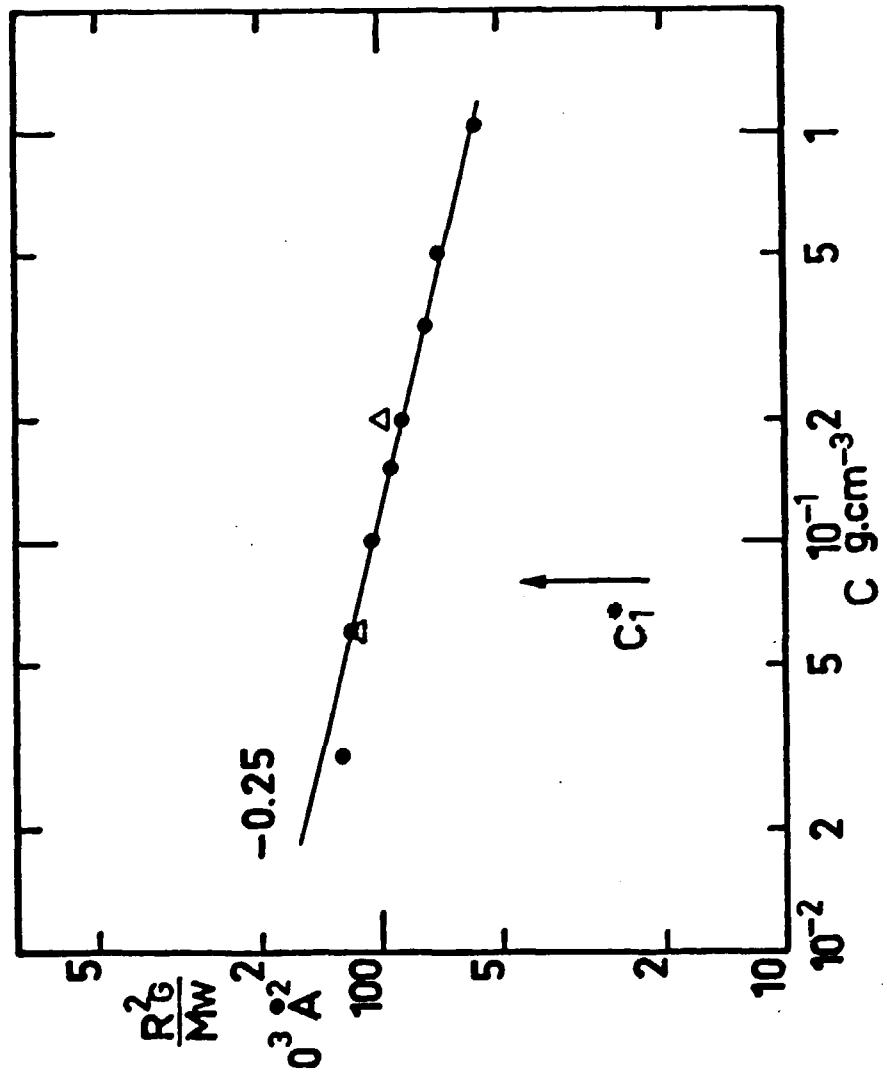
$$C_s = 1,47 \cdot 10^{-3} \text{ gcm}^{-3}$$



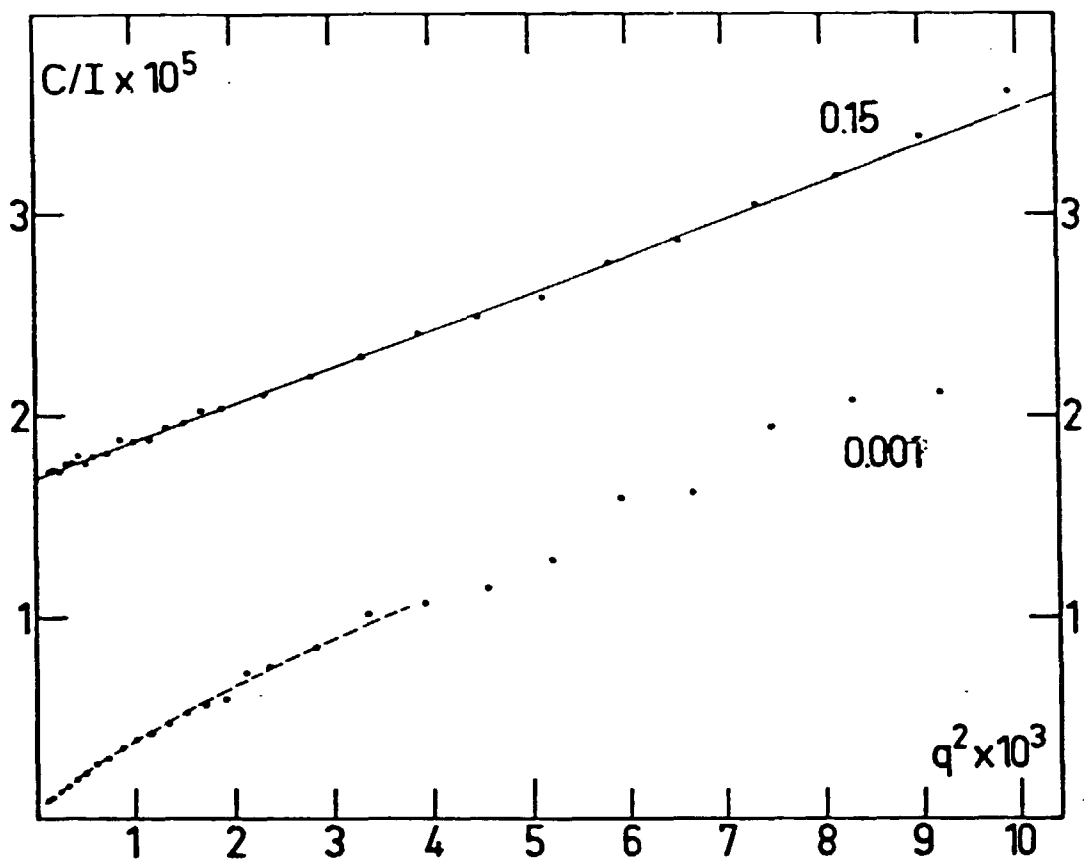
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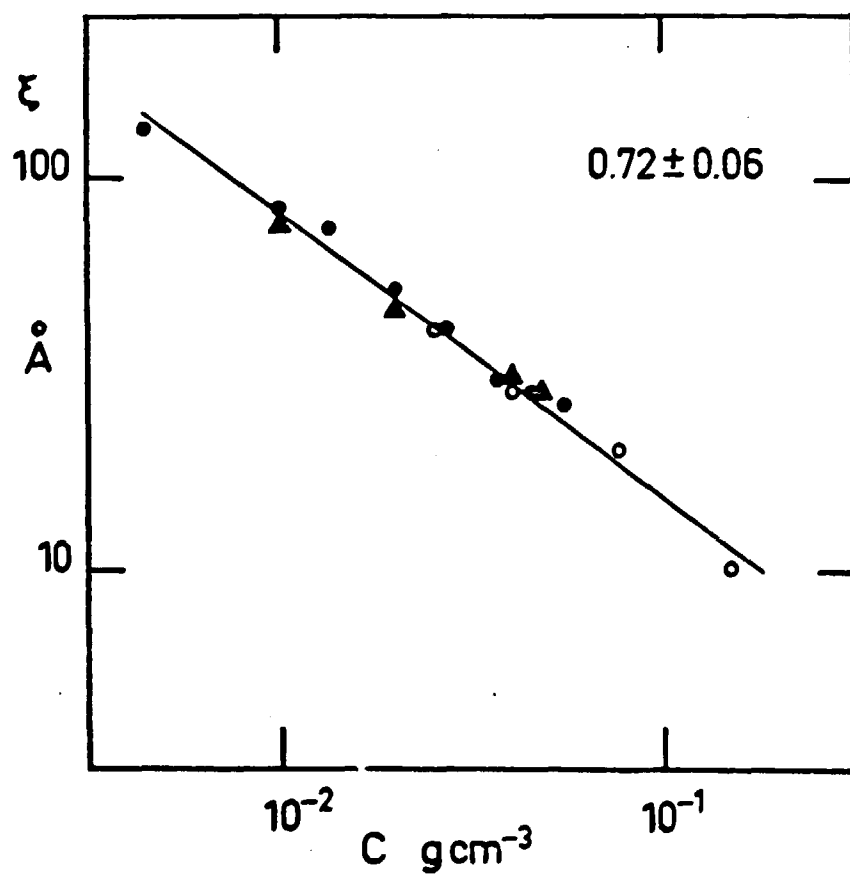
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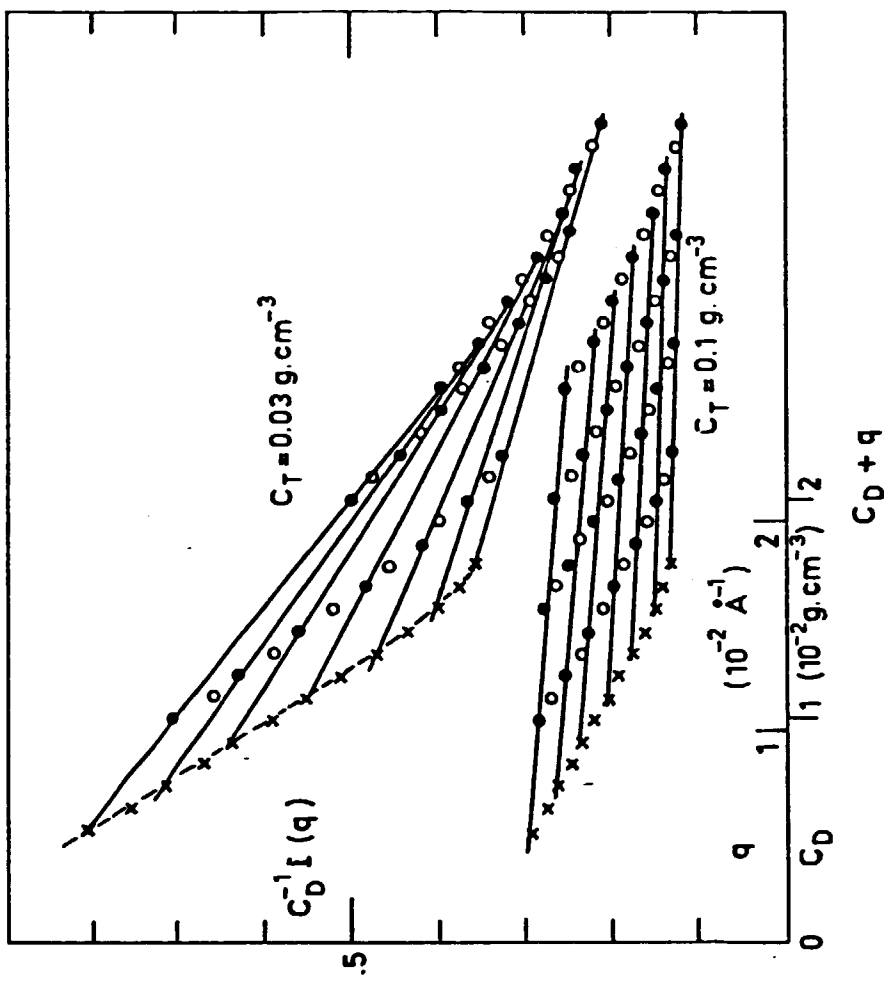
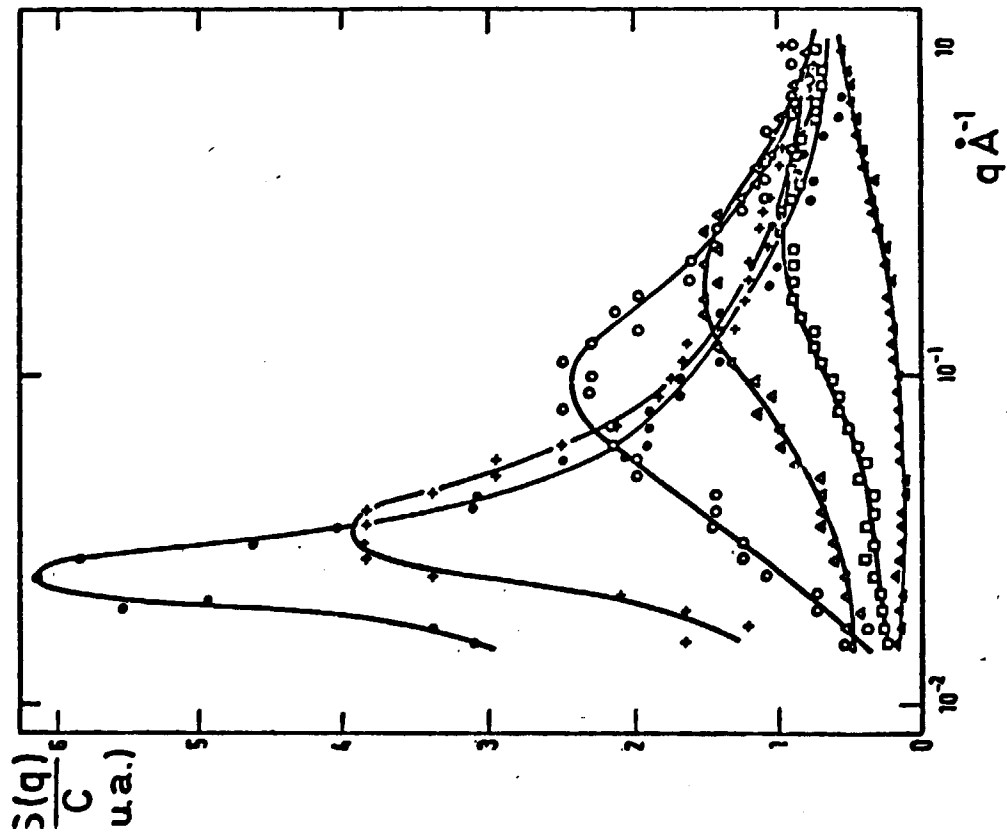
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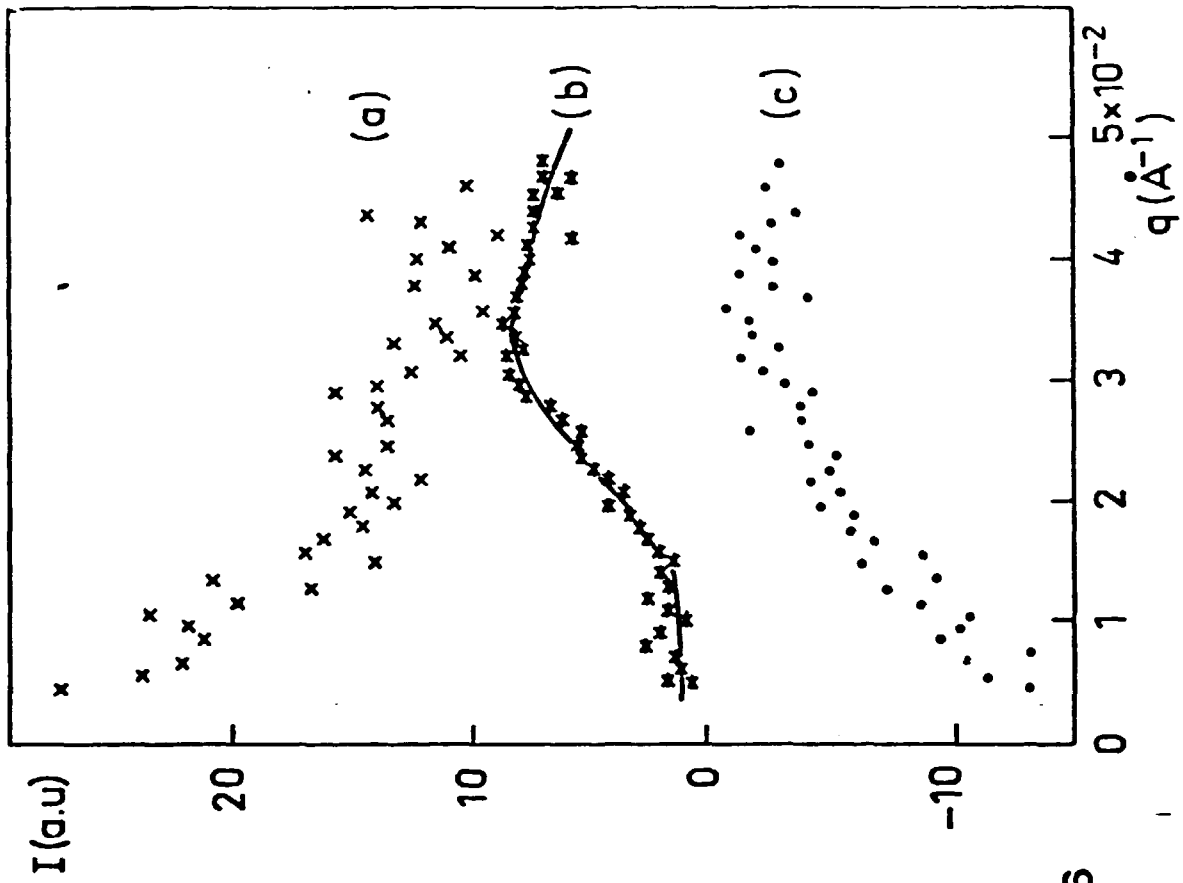


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