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SMALL-ANGLE NEUTRON SCATTERING INVESTIGATION OF POLYMER SYSTEMS

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Introduction

Small-angle neutron scattering (SANS) has proved to be a powerful method for investigation of structure features of colloidal size (10^1 - 10^3 Å). The field of applications of this technique overlaps to some extent with that of small-angle X-ray scattering (SAXS). There are several advantages of neutrons compared to X-rays, such as sensitivity to magnetic structures, low absorption for most materials, and possibility of isotope labeling. Thanks to the last advantage, SANS has become an indispensable tool for characterizing the structure of polymeric materials.

The SANS has been applied to polymers since the early seventies. Several papers concerning conformations of polymer chains in the bulk state appeared [1-4]. The experiments confirmed the Flory hypothesis that the chain dimensions in the bulk are the same as those in Θ solvents.

First SANS experiments in the Joint Institute for Nuclear Research (JINR) Dubna were performed in the mid-1970s [5]. Construction of the IBR-2 pulse reactor and its start in the early eighties strongly motivated developing a time-of-flight SANS spectrometer based on this source. This contribution is intended to trace the employment of SANS in structure studies on polymeric system. In the first decade, these studies as well as development of the instrumental equipment and experimental procedures were closely associated with the activities of Yu.M. Ostanevich.

Experimental procedures

It is well known that scattering intensity can be expressed as a function of the scattering vector. Its magnitude depends on the scattering angle 2θ and the neutron wavelength λ as $q = (4\pi / \lambda)\sin\theta$. For the spectrometers attached to pulse sources, a time-of-flight (TOF) method is used for data collection. At fixed scattering angles, the scattered neutrons are detected and sorted according to their time of arrival. The times of arrival can be easily transformed in neutron wavelengths. The TOF technique makes it possible to measure scattering intensities within a wide q-range simultaneously. This advantage is at the expense of some complications consisting in the wavelength dependence of the relevant characteristics of the scattering process (intensity of incident beam, sample transmission, detector efficiency) which have to be taken into account when calculating the scattering intensity from the raw data. An elegant way of solving this problem developed in Dubna has been described by Ostanevich [6].

Two sets of data are recorded for each sample: (1) scattering from the sample alone (I_S), (2) scattering from the sample and from a vanadium standard placed in the primary beam between the sample and detector (I_{SV}). Combination of these data sets leads to relative scattering intensity from the sample without determination of wavelength-dependent intensity of the incident beam, the sample transmission and the detector efficiency. This procedure was later improved to provide scattering intensity on an absolute scale. The formula for the scattering cross-section per unit volume of a sample with thickness d is [7]

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(q) = \frac{I_\mathrm{S}}{I_\mathrm{SV} - I_\mathrm{S}} \frac{\Omega_\mathrm{V}}{\Omega_\mathrm{S}} \frac{T_\mathrm{V} d_\mathrm{V}}{d} \left(\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right)_\mathrm{V} \qquad (1)$$

where Ω_S and Ω_V are the solid angles at which the detector is seen from the position of the sample and standard, respectively T_V, d_V and $(\mathrm{d}\,\Sigma\,/\,\mathrm{d}\Omega)_\mathrm{V}$ are the transmission, thickness and scattering cross-section of the vanadium standard, respectively.

A program based on ideas of Yu. M. Ostanevich performing all necessary steps from the raw data to the scattering curve was written by V. Yu. Bezzabotnov in the early eighties and is still in use [8].

Polyelectrolyte solutions

Polyelectrolytes are polymers bearing ionizable groups. Usually they have one ionizable group in every monomeric unit. The charge of polyion is compensated by small ions with the opposite charge (counterions). The presence of charges has a strong effect on the supermolecular structure, conformation of polyions, and also on the structure of the solvent in their vicinity. All these structure levels have been probed by means of small-angle neutron scattering.

Small-angle scattering curves of polyelectrolyte solutions exhibit a broad maximum, the position of which depends on the polyelectrolyte concentration and charge density. Figure 1 shows examples of such curves. To explain the occurrence of this maximum, various structure models have been proposed. A cylindrical model [9-11] assumed the existence of a local parallel arrangement of polyions. De Gennes and coworkers [12] suggested an isotropic model assuming partly flexible chains oriented randomly. The model proposed by Ise and Okubo [13] assumed that the maximum arises due to a three-dimensional ordering of polymer coils.

Investigation of polyelectrolytes solution using SANS started in the early eighties. This investigation has been supported by the results of SAXS experiments performed at the Institute of Macromolecular Chemistry, Prague (IMC). These studies were primarily aimed at the elucidation of the supermolecular structure of polyelectrolyte solutions. However, it became clear soon that one cannot interpret the SANS and SAXS data without comprehending how various interactions between the system components (polyions, counterions, solvent) are reflected in the scattering behaviour. This leads us to studies devoted to hydration of polyions, their local structure and size, binding of counterions to polyions and, finally, to interpolyion correlations.

A vast majority of our studies deals with poly(methacrylic acid) (PMA), a weak polyacid, the charge density of which can be easily controlled by adding of an alkali metal hydroxide (e.g., NaOH) and characterized by the degree of neutralization α (= the number of hydroxide molecules per one monomeric unit of polyacid).

Hydration and local structure of polyions, binding of counterions [7,14,15]

Figure 1 shows SANS and SAXS curves of PMA at various degrees of neutralization, α. We can see that with increasing α, neutron intensities decrease, while for the X-radiation (at least at high q), the opposite trend is observed. This behaviour can be explained by the existence of a hydration layer that surrounds the polyion and inside which water molecules are arranged more closely than in the bulk water [14]. A more detailed analysis of the scattering curves [7] reveals that at full ionization ($\alpha = 1$), the PMA polyion is enveloped by a monomolecular shell of hydration water which contains about 18 water molecules per one monomer unit of PMA. The density of hydration water is higher than that of normal water by ~ 8%.

The SANS curves can also provide information about the stiffness of polyions. The relevant parameter is the persistence length, L_p. The higher stiffness, the larger L_p. Figure 2 shows the persistence length of PMA as a function of degree of neutralization.

The persistence length is given by interactions of several adjacent monomeric units. Its constant value for $\alpha \leq 0.2$ may be explained by a low probability of the occurrence of two or more adjoining charged groups. In such a case, electrostatic interactions have only weak influence on the local structure of polyions. At increased charge densities, the electrostatic interactions between charged groups become operative and L_p increases. At high α (> 0.5), the charge density of polyions does not increase any longer with increasing α due to the phenomenon known as counterion condensation, and, consequently, L_p also remains unchanged.

The condensation occurs as a result of electrostatic attraction of counterions to polyions. According to Manning's hypothesis [16], the charge density of polyion cannot increase arbitrarily upon neutralization. If the mean distance between the charges along the chain is reduced to a critical value (about 7 Å for univalent counterions), further neutralizaton leads to condensation of counterions on polyions. The condensed counterions compensate the additional charges on the polyions and the mean distance between the net charges is kept at its critical value.

The number of condensed (bound) counterions has been determined in two ways. In [7] a procedure based on comparison of the SAXS and SANS intensities was employed. Later on, we proposed a novel procedure based on the determination of the excess scattering amplitude from

SANS or SAXS data [15]. The excess scattering amplitude is sensitive to the binding of low-molar-mass compounds to macromolecules. The results obtained using the latter procedure for Na^+ counterions in PMA solution (Fig. 3) are in good agreement with the predictions of Manning's theory.

Size of polyions, interpolyion correlations [17,18]

Scattering intensity for a solution of macromolecules can be written as the sum of two contributions, one coming from single particle (intra) and the second arising as a result of interference of the waves scattered on different particles (inter). The first contribution contains information on the shape and size of single particles, while the second depends also on spatial arrangement of the particles. Reliable structure information can be extracted from the scattering data if the two contributions can be separated.

For polymers, there exists a simple way of separating the intra- and interparticle contributions if a pair of normal and deuterated polymer of the same length is available. The intensity scattered from an incompressible solution of normal (H) and deuterated (D) macromolecules can be written as [19-21]

$$I(q) = (a_D - a_H)^2 c_D(1 - c_D)P(q) + (a_P - a_0)^2[P(q) + Q(q)] \qquad (2)$$

where the scattering functions $P(q)$ and $Q(q)$ come from intramolecular and intermolecular interferences, respectively, a_D, a_H and a_0 are the scattering lengths of the deuterated monomer, normal monomer and solvent, respectively. The mean scattering length of monomer is $a_P=c_Da_D+(1-c_D)a_H$, where c_D is the fraction of monomers that are deuterated.

To extract the scattering functions using Eq. 2, we measured scattering intensities for $c_D = 0$ (normal polymer), $c_D = 1$ (deuterated polymer) and $c_D = (a_0-a_H)/(a_D-a_H)$ (the mixture of normal and deuterated polymers with $a_P = a_0$). This was done for several degrees of neutralization; an example is shown in Fig. 4. The SANS curves of the solutions with deuterated or normal polyions show the well-known maximum indicating a strong interference effect. For a mixture with the above given fraction of deuterated molecules, however, the scattering intensity decreases monotonically with increasing q, as expected for single-polyion scattering function.

The $P(q)$ function was used for determination of the size of polyions [17]. The size was characterized by two radii of gyration. Their variation with degree of neutralization is shown in Fig. 5. R_{w0} was calculated from the persistence length (L_p) and the contour length of the polyions (L) as $R_{w0}^2 = LL_p/3$ corresponding to an unperturbed polymer coil without long-range interactions between their segments. R_w is the actual radius of gyration determined from the innermost part of the intramolecular scattering function.

At $\alpha=0$, the two radii are equal within experimental error. This means that the non-ionised PMA chains are in the unperturbed state. The appearance of charges leads to expansion of the polyions. At low α (≤ 0.2), only long-range repulsive interactions are important ($R_{w,0}$ = const), while at $\alpha > 0.2$, both short- and long-range interactions are operative. For $\alpha > 0.5$, no variation of R_w and R_{w0} with α is observed. This again can be explained by condensation of counterions. The charge density is stabilized, and so are the electrostatic interactions.

The interparticle function Q(q) was calculated as a combination of the three experimental SANS intensities mentioned above [18]. Q(q) was then transformed into $N(r)/N$, a relative concentration of monomer units belonging to foreign macromolecules in the vicinity of a reference monomer unit (Fig.6). This function describes the intermolecular correlations. Due to repelling of the charged segments, $N(r)/N$ is smaller than unity near the origin. With increasing r, $N(r)/N$ monotonically increases and reaches unity at r = 120-150 Å. No oscillations, which would indicate an ordered structure, are observed. These features of the experimental correlation functions are in agreement with those suggested by de Gennes on the basis of the correlation hole concept [22].

Ise and Okubo proposed a model with a three-dimensional ordering of the polyelectrolyte coils [13]. In ref. [23], we published an alternative interpretation of the experimental findings to that which led these authors to proposal of their model.

Swollen polymers and gels

Unlike polymers in solution, solid polymers are not frequently studied using the SANS technique. The reasons are insufficient contrast and high incoherent background for hydrogenouous polymers. Much more favourable conditions can be achieved for polymers in the swollen state. Choice of a deuterated swelling agent strongly enhances the scattering contrast and facilitates both the data acquisition and their interpretation.

Thermosensitive gels [24,25]

Some polymer gels (swollen polymer networks) are sensitive to environmental conditions. As a result of the change in temperature, pH, solvent quality or other conditions, phase transitions can take place. Using SANS we studied temperature-induced structure changes of poly(*N*,*N*-diethylacrylamide) (PDEAAm) networks swollen with D_2O. PDEAAm networks with a small number of charged monomeric units (5 molar % of sodium methacrylate (MNa)) were also studied [23].

In small-angle scattering experiments a power-law decay ($\sim q^{-S}$) of the scattering intensity is frequently encountered. The value of the exponent S depends on the type of structure. Figure 7 shows the temperature dependence of the characteristic exponent. At low temperatures, the exponents are approximately 2. This value is typical of polymer coils and swollen networks. The larger S values observed at high temperatures ($S \approx 4$) indicate the presence of compact structures. Thus, the observed change in the exponent reflects the transition from the expanded to collapsed state.

Beside the PDEAAm gels in equilibrium, also the structure changes after temperature jumps have been followed by a time-resolved SANS experiment [24]. Evolution of the SANS curves after two temperature jumps (from 25 to 30 °C, from 30 to 35 °C) is shown in Fig. 8. Analysis of the data indicates that, after both T-jumps, the hydrogel contains two phases, differing in their polymer contents. The dense phase corresponds to the equilibrium structure at the final temperature. The character of the non-equilibrium, dilute phase, formed after the T-jump from 25 to 30 °C, is different from that after the jump from 30 to 35 °C. In the former case, the polymer content in the dilute phase is high enough to give rise to Lorentzian-type scattering which is typical of swollen networks. In the latter case, the excess water is probably present as droplets roughly 2000 Å in diameter, with a minimum polymer content.

Nylon-6 in swollen state [26]

This part concerns with an unusual application of small-angle scattering. We studied a semicrystalline polymer (Nylon-6) swollen to various degree with D_2O to gain information about the structure of the amorphous phase [26]. The study was based on the determination of the mean-square fluctuation of scattering density

$$\overline{(\Delta\rho)^2} = \frac{1}{2\pi^2}\int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q)\,dq \qquad (3)$$

and a comparison with the theoretical results calculated for available structure models of swollen Nylon. The best agreement with the experimental data was obtained for the model with inhomogeneously distributed water in the amorphous phase and having the maximum concentration at the centre of the amorphous layers.

Block copolymer micelles

Block copolymer micelles are polymolecular particles with a dense core formed by insoluble blocks and a protective corona formed by swollen soluble blocks. The micelles have attracted considerable attention both for theoretical interest and their potential applications.

Simple core / corona micelles [27-32]

Most of the micelles studied so far have a simple core /corona structure formed by an AB or ABA block copolymer. The SANS can provide information both on the micelle as a whole and on its internal structure. For a wide class of micelles, a simple approach based on the bare-core approximation (BCA, see below) of the SANS curve can be employed. Most prospective applications of the micelles are based on loading sparingly soluble compounds into micellar cores (solubilization). This phenomenon can also be studied by SANS because this method is sensitive to the core characteristics.

Structures of the micelles formed by the following hydrophobic/hydrophilic block copolymers in aqueous media have been studied:

poly(oxyethylene)-*block*-poly(oxypropylene)-*block*- poly(oxyethylene) [27]
poly(methyl methacrylate)-*block*-poly(acrylic acid) [28,29]
poly(sulfobetaine)-based block copolymers [30]
poly(2-ethylhexyl acrylate)-*block*-poly(acrylic acid) [31]
poly(dodecyl methacrylate)-*block*- poly(acrylic acid) [32]

In papers [28, 31, 32] by Kříž et al., the SANS technique has provided information on the structure of the micelles studied, but the papers are primarily aimed at the elucidation of polymer dynamics in micellar systems as seen by NMR methods.

Three-layer (onion) micelles

As already mentioned, in potential applications, the uptake and release of poorly soluble compounds into or from micellar core play an important role. It is desirable to have a possibility of controlling these processes. Promising candidates for such purpose are three-layer (onion) micelles. Kříž et al. [33] prepared such micelles from an ABC block copolymer (poly(2-ethylhexyl acrylate)-*block*-poly(methyl methacrylate)-*block*-poly(acrylic acid)). Their study includes the first attempt to characterize onion-type micelles using SANS.

In ref. [34], a polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PS-*b*-PVP-*b*-PEO) was used to prepare three-layered micelles. The pH-induced structure changes of these micelles were studied by means of SANS. The results demonstrate that at high pH, the middle, PVP, blocks are in the collapsed state and form an outer part of the micelle core, while at low pH, these blocks are swollen. This gives a possibility of controlling the transport into or from the micelle cores by variation of pH.

Nanoparticles based on block copolymer micelles

Another type of three-layer nano-sized particles was studied in refs. [35-37]. The particles were prepared by adding methyl methacrylate (MMA) monomer to a polystyrene-*block*-poly(methacrylic acid) (PS-*b*-PMA) micellar solution in aqueous medium and subsequent polymerization. The contrast-matching SANS experiments [35, 36] revealed that upon polymerization, the PMA chains form a layer on the surface of the PS cores of the original micelles. Figure 9 shows how this process is reflected in scattering behaviour.

Novel interpretation procedures

The SANS experiments performed in Dubna not only provided valuable information on the structure of the polymer systems studied but their results also serve as an inspiration for suggestion of novel interpretation procedures.

Molecular weight determination without using absolute intensities and contrast

The conventional procedure for the determination of molecular weight using scattering methods is based on formula

$$M_\mathrm{w} = \frac{N_\mathrm{A}}{c(\Delta b)^2}\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0) \qquad (4)$$

where c is the particle concentration, N_A is the Avogadro number and Δb is the excess scattering amplitude (contrast). Thus the methods uses absolute intensities and the contrast factor. We have shown that the latter characteristic can be expressed through the integrated scattering intensity [38]. The next step was a new formula for the determination of M_w

$$M_\mathrm{w} = -\frac{2\pi^2 N_\mathrm{A} I(0)}{c\dfrac{\mathrm{d}}{\mathrm{d}c}\displaystyle\int_0^{q_\mathrm{m}}\frac{I(q)}{c}q^2\mathrm{d}q} \qquad (5)$$

where $I(q)/c$ is the scattering intensity on an arbitrary scale normalized to unit concentration and q_m is the q value above which this normalized intensity does not depend on concentration. Using Eq. 4 one can calculate M_w from the scattering curves measured at two or more particle concentrations. Unlike the conventional procedure, this method does not require putting the intensities on an absolute scale and determining the contrast. Thus it can be used also if the chemical composition and/or the partial volume of the particles are not known. Examples of applications of the method illustrating its advantages and limitations are given in ref. [39].

Bare-core approximation

It was shown [40] that the middle part of a small-angle scattering curve of block copolymer micelles with a core/corona structure can frequently be satisfactorily described by the scattering function of spherical particles (bare-core approximation, BCA). This makes it possible to easily determine structure characteristics (mean radius, polydispersity, volume, mass) of the micelle core. The BCA is not a universal approach, but it can be used if the micelle has sufficiently larger dimensions than the core and its excess scattering amplitude is not too high in comparison with that of the core. For SANS studies of the micelles formed by a normal (hydrogenous) copolymer in a deuterated solvent, these conditions are usually met.

The BCA approach can be also used if the excess scattering amplitudes of the core and corona are not a priori known or if reliable data for the innermost part of the scattering curve are not available. These circumstances usually make the use of a more sophisticated, many-parameter, micelle model difficult or impossible.

Concluding remarks

Most of the investigations conducted in the 1990s in co-operation of the JINR Dubna with the IMC Prague were devoted to block copolymer micelles. Though these studies were performed without direct participation of Yu. M. Ostanevich, they still benefited from the results of his work.

It follows from a comparison with the data obtained using the D11 spectrometer in the ILL Grenoble (Fig. 9) that the YuMO spectrometer, constructed and equipped with the data reduction procedures using the ideas proposed by Yu. M. Ostanevich, provides SANS data of good quality.

Recently, Prof. Khokhlov and his coworkers began to perform SANS experiments on polymer systems in Dubna. One can expect that interesting papers based on these experiments will appear soon.

Acknowledgment

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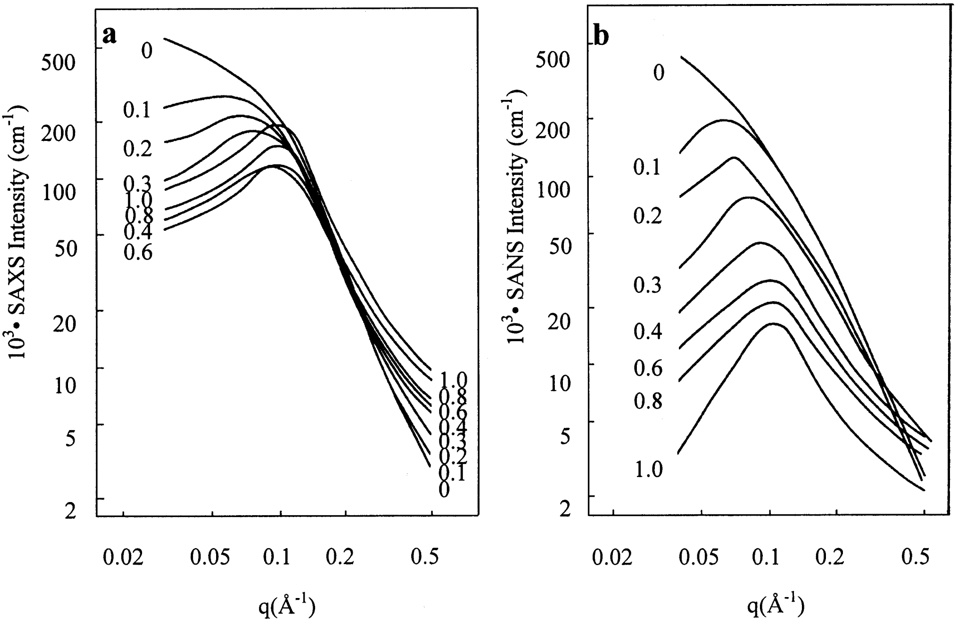

Figure 1 SAXS (a) and SANS (b) curves of PMA in D_2O at various degrees of neutralization α.

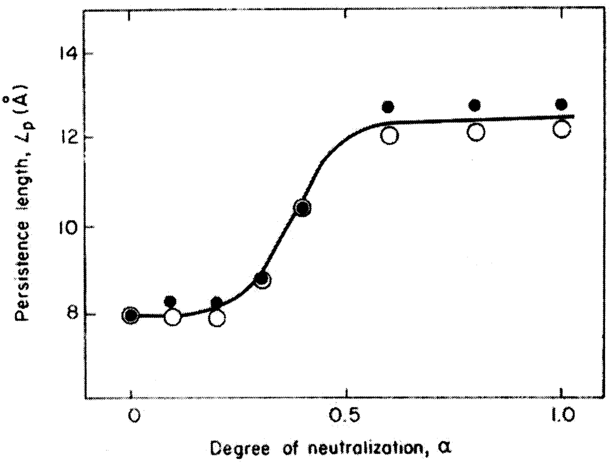

Figure 2 Variation of the persistence length of PMA with the degree of neutralization: (○) Na^+ counterions, (●) Li^+ counterions.

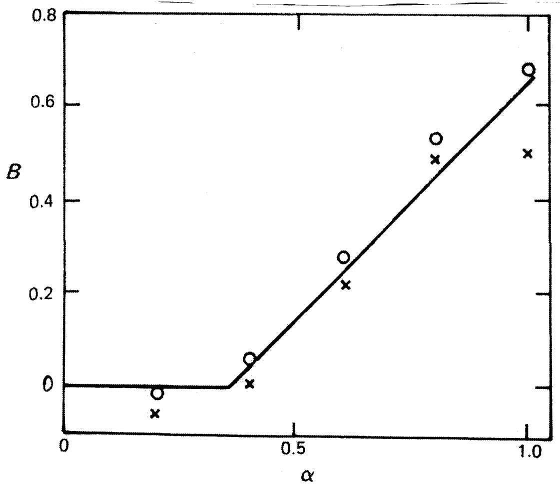

Figure 3 The number of Na^+ counterions bound to one monomeric unit of PMA, determined from desmeared (x) and smeared (○) SAXS data at various degrees of neutralization.

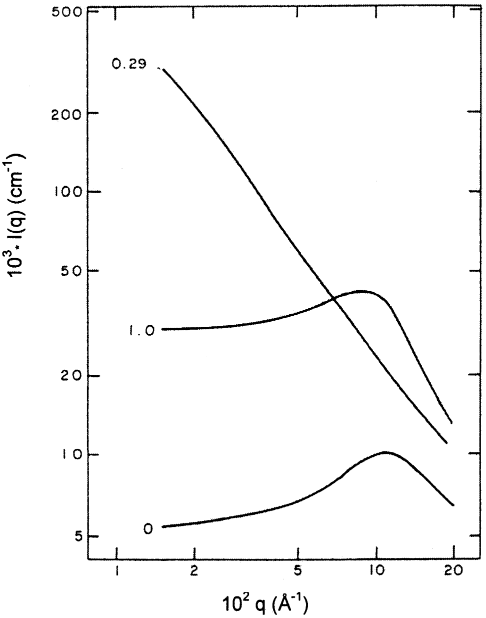

Figure 4 SANS curves of PMA(H), PMA(D), and of their mixture , in D_2O; degree of neutralization α = 1. For the fraction of deuterated polymer $c_D = 0.29$, the mean scattering density of polymer matches that of the solvent and single-polyion scattering is observed.

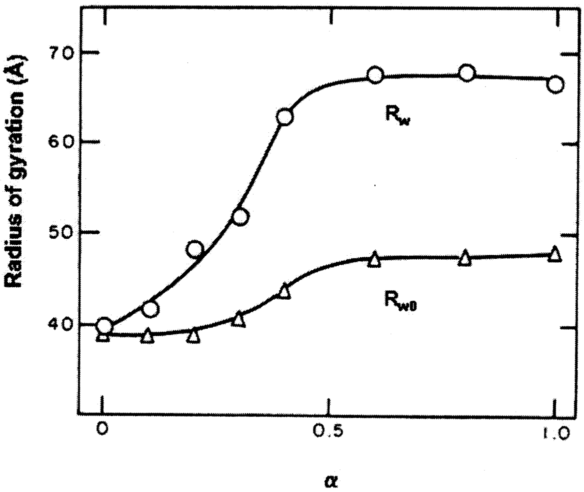

Figure 5 Variation of the actual (○) and unperturbed (Δ) radii of gyration of PMA polyions with the degree of neutralization.

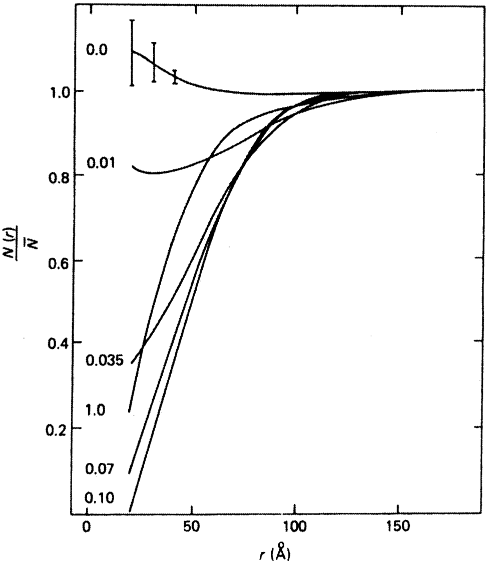

Figure 6 Intermolecular scattering function of PMA at various degrees of neutralization.

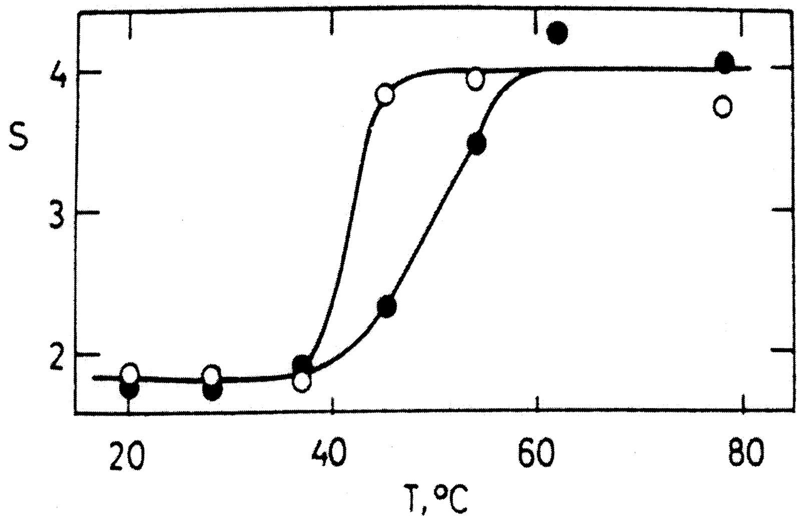

Figure 7 Temperature dependence of the exponent *S* in a power-law decay ($I \sim q^{-S}$) of SANS intensity for PDEAAm (○) and P(DEAAm + MNa) (●) networks swollen with D_2O.

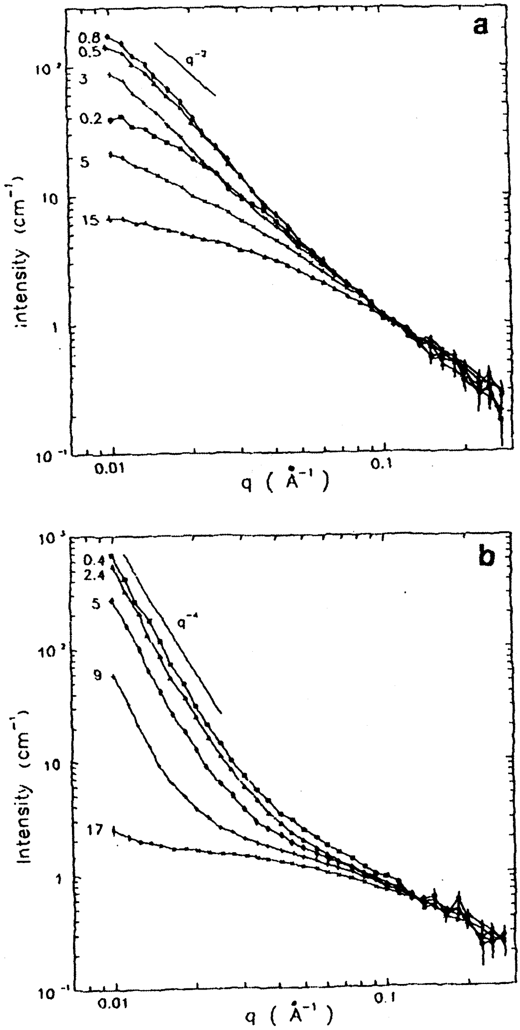

Figure 8 Time variation of SANS curves of PDEAAm hydrogel after temperature jumps from 25 to 30 °C (a) and 30 to 35 °C (b). The numbers denote time elapsed in hours.

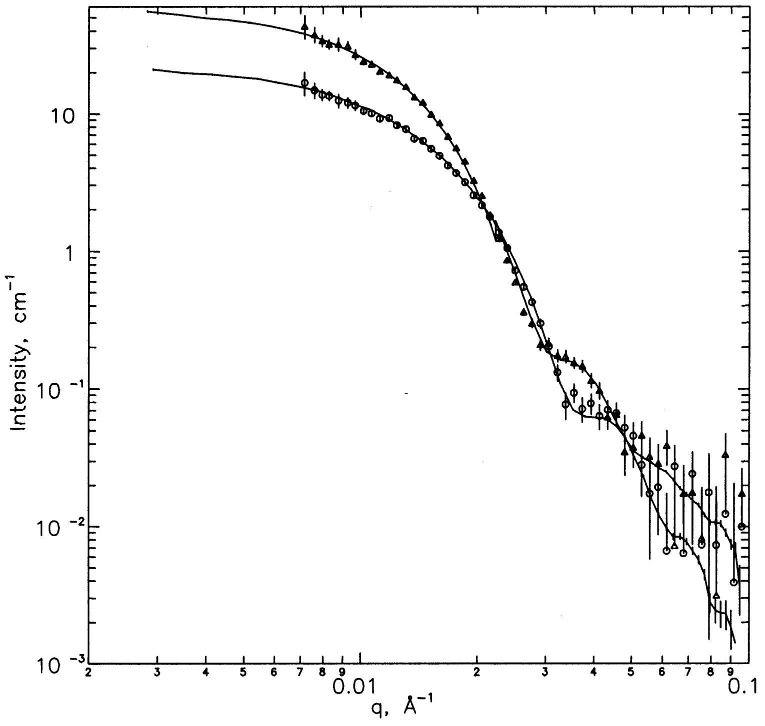

Figure 9 SANS curves of PS/PMA micelles (o) and PS/PMMA/PMA nanoparticles (Δ) measured on the YuMO spectrometer. Micelle concentration 1.1×10^{-3} g/ml, MMA monomer concentration 4.0×10^{-3} g/ml. Solid lines: measured on the D11, ILL, Grenoble.

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Сделан обзор исследований полимеров методом малоуглового рассеяния нейтронов, выполненных в течение 1980–1990 гг. в Объединенном институте ядерных исследований в сотрудничестве с Институтом макромолекулярной химии (Прага, Чешская Республика).

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Small-Angle Neutron Scattering Investigation
of Polymer Systems

Small-angle neutron scattering investigation of polymer systems performed in 1980–1990 at the Joint Institute for Nuclear Research in co-operation with the Institute of Macromolecular Chemistry (Prague, Czech Republic) is reviewed.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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