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Aggregation of monocarboxylic polymer chains by neutralization. Neutron and X ray scattering

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Résumé. — On étudie les agrégats formés au cours de la neutralisation, en solvant organique, d'une chaîne de polymère ayant un acide carboxylique terminal. La diffusion des neutrons et la diffusion des rayons X aux petits angles sont utilisées pour la caractérisation d'une part des agrégats, d'autre part de leur structure en fonction de la concentration.

Abstract. — The aggregates obtained by the neutralization of a carboxylic single-ended polymer chain in organic solvent are studied. Neutron and X-ray small angle scattering are used for the characterisation of the aggregates and for the study of their structure as a function of concentration.

Introduction.

Ionomers are polymeric materials in which ionized groups have been distributed at random along the polymeric chains. The ionized groups may be acid functions neutralized by metal cations. Because they find themselves in an apolar matrix, they tend to cluster into multiplets or into larger domains [1] which contain a high density of cations. These clusters link the chains together, making the material insoluble in most solvents, this crosslinking has important consequences for most of the properties of the material. Mechanical properties, glass transition temperature, ion exchange properties and also optical properties are commonly affected [2, 3].

These ionomers are difficult to study, precisely because of the crosslinking which prevents solution studies, indeed the interpretation of solid state properties is substantially more complex. For this reason it would be advantageous to start with a simpler system where the effects of the cations and those of the polymer would be decoupled to some extent.

A step in this direction was made with the synthesis by Broze, Jerome and Teyssier [4, 5, 6] of halatotelechelic polymers which contain only two acid groups per macromolecule, one at each end of the chain. Again when these end groups are neutralized, they cluster into ionic domains which link many chains together. The resulting networks can be

swollen in a variety of solvents. They will be characterized by the nature of their counterions, the length of the chains which connect two ionic clusters and the swelling ratio.

Still the study of such gels remains difficult because the functionality (aggregation number) of the crosslinks (junction, cluster) cannot be readily determined, and also because the configurations of the chain result from a combination of local constraints (crowding of chains near a ionic cluster) and network constraints (stretching of chains between two crosslinks).

Thus the formation of a crosslinked network greatly complicates the problem, firstly because it inhibits solubility and secondly because it influences chain configurations. It is possible to do away with the network by taking macromolecules which carry only one ionizable end group. We expect that, when such macromolecules are neutralized, they will form star-like aggregates where f branches, of N monomers each, will radiate from a central ionic cluster.

Because such star-like aggregates can be diluted and separated from each other in a solvent of the polymer chains, their parameters should be accessible through classical methods. For example, the molecular weight M_s of the star may be measured and compared with that of a single monoacid macromolecule M_b . This will yield the number f of branches in a star, which may be studied as a function of the type of cation, of the molecular

weight of one branch and of the stoichiometry of the neutralization.

Moreover the configurations of individual branches in a star are accessible through the isotopic labelling method in small angle neutron scattering experiments. The configurational statistics of such stars are important because they may serve as models for more complicated problems such as networks and polymer adsorption. They have been studied theoretically by Cotton and Daoud [7], then by other authors using similar models [8, 9].

The physico chemical requirements for the star forming polymer are that it should be a well known polymer, easily synthesized and resistant to chemical degradation. We choose a monocarboxylated polystyrene whose chains are linear and have molecular weights of either 6 000 ⁽¹⁾ or 30 000. The number of acid groups per chain is 0.96 and 0.95 respectively. These amounts of acid are obtained only on the polymer which has been fractionated. Actually in the synthesis of such a material, coupled linear and three armed star results in side reactions. This could be easily observed by GPC on the 30 000 molecular weight, polymer for which a large shoulder around 60 000 Dalton is shown by the chromatogram. About 20 % of the polymer is concerned by this bump, which is easily removed by fractionation. Polymers are neutralized through the technique described by Jérôme [10], where the acid polymer and the salt are both dissolved in an organic solvent. Various cations have been used for the neutralization ; Ba, Al, Zn, K, Mg, the choice being made according to the properties obtained with the same cation in the case of halatotelechelic polymers [2, 10, 11]. Hence we assume that they will provide us with stars which will not dissociate when dissolved in the solvent.

The solvent should be a good solvent of the polymer chains so that individual stars are separated in a dilution experiment. It should also be non-polar, so that the clusters which link the polymer in the star like aggregates will not dissociate. We choose toluene, which meets all these requirements.

Our original aim was to determine the molecular weight of individual stars for which we expected that a light scattering experiment would be appropriate. In the end we found that the objects detected by light scattering may not be the individual stars we expected. This forced us to look at shorter scales where the dimension and distances of individual stars might show up. Accordingly we used small angle neutron scattering (SANS) and small angle X ray scattering (SAXS) to study correlations in the range 5×10^{-2} to 0.5 \AA^{-1} . The results of all three types of experiments are reported here.

⁽¹⁾ The 6 000 Dalton polymer has been synthesised in Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Liège Belgium.

Choice of experimental conditions.

The interaction of radiation with matter occurs at the level of scattering centers, which may be electron clouds, individual atoms or nuclei, depending on the type of radiation used. Waves scattered by different scattering centers will interfere with each other. The relevant phase difference is determined by the scalar product qr , where q is the magnitude of the scattering vector :

$$q = 4 \pi / \lambda \times \sin \theta / 2 ,$$

θ being the scattering angle

λ the wavelength of incident radiation

r the vector joining scattering centers

The resulting interference pattern reflects the spatial distribution of scattering centers in the irradiated volume. Small-angle scattering corresponds to values of q small enough that significant phase differences only occur for large distances r , then the scattering pattern reflects fluctuations in the density of scattering length throughout the irradiated volume.

If the material is made of large objects dispersed in a uniform medium, the interferences can be separated in two classes :

(a) interferences between scattering centers which belong to the same object, the object being a part of space in which the density of scattering center of one species may be considered as continuous. These interferences are determined by the shape and internal structure of the object. They are described by a form factor $S_s(q)$, which is related to a distance distribution function $G_s(r)$. Generally we refer to this contribution by calling it the intracorrelation term ;

(b) interferences between scattering centers which belong to different objects. These interferences result from correlations between the relative locations of the objects. They are described by a structure factor $S_d(q)$, which is related to a pair correlation function $G_d(r)$. We will refer to this contribution by calling it the intercorrelation term.

In the experimental scattering pattern, the relative weights of these two types of interferences depend on the concentration c of the distinct objects in the medium, following the subsequent relation

$$I(q) \approx c S_s(q) + c^2 S_d(q) . \quad (1)$$

Starting from this relation it can be seen that, if the objects remain unchanged in a dilution experiment, the self term $S_s(q)$ remains unchanged and then both the self term and the distinct term $S_d(q)$ can be extracted from measurements of $I(q)$ at different concentrations c . If the conformation of the object changes through dilution, the scattering function of an isolated object can still be

extracted from an extrapolation to vanishing concentration through a Zimm plot.

However when dealing with association structures as in our case, one must obviously require that the objects may not dissociate in a dilution experiment. Keeping in mind these technical and material conditions we can now define the range of concentrations which may be useful for determining the characteristics of individual aggregates. The upper limit of this range should be the overlap concentration c^* , beyond which neighbouring objects come in contact or interpenetrate. Since we do not know the dimensions of individual objects, we cannot calculate c^* *a priori* and its value must be estimated.

Our system may be considered as a part of a halatotelechelic network in which all the chains have been spliced in their middle, all the other parameters being kept in this operation. Through this procedure the network is transformed into an array of stars. The radius of gyration of these stars can be estimated through the mean field model, which relates the radius of gyration of the star R_s to the radius of gyration of a single branch, and to the number of branches [12] according to the relation :

$$R_s = (3 - 2/f)^{1/2} R_b. \quad (2)$$

This yields c^* as a function of f and of the molecular weight of one branch M_b .

$$c^* = \frac{f^{1/2} M_b}{4 \pi N (3f - 2)^{3/2} R_b^3} \quad (3)$$

where N is the Avogadro number.

Here we assume that f must be at least equal or greater than 3, hence :

$$\begin{aligned} \text{if } f = 3 & \quad c_s^* = 0.87 c_b^* \\ \text{if } f > 4 & \quad c_s^* > c_b^* . \end{aligned}$$

These lead to an evaluation of c^* of

$$\begin{aligned} c^* &\approx 17 \% & \text{for } M_b = 6\,000 \\ c^* &\approx 6 \% & \text{for } M_b = 30\,000 . \end{aligned}$$

In practice, in order to be well away from the c^* concentration, we have used solutions at concen-

trations approximately ten times lower than c^* . These solutions are again diluted for the Zimm-plot and then are in the range $0.0025 < c < 0.01$ g/ml.

Results from GPC and light scattering (LS).

In a first step we used classical techniques in an attempt to determine the average molecular weight of the aggregates. Four neutralized polymers were used, named PS-Zn 6 000, PS-Ba 6 000, PS Zn 30 000 and PS-Ba 30 000. In this notation the nature of the polymer is indicated first, followed by that of the counterion and lastly the molecular weight of the polymer. They are studied together with the acid polymers, named in the same way PS-COOH 6 000 and PS-COOH 30 000.

In the Gel Permeation Chromatography technique (GPC), identical results were obtained for the neutralized star forming polymer and for the acid non-aggregating polymer. The significance of this result is ambiguous. It could be that a single branch has the same elution volume as the whole star [13] (even though their molecular weights are quite different). Or more likely, because of a low cohesion energy, the clusters may dissociate in the shear gradient of the GPC column.

At this stage we turned to LS. For the non-associated acid polymer this yields the same molecular weight values as the GPC results, these values are shown in table I together with the viscosity results for the molecular weight in dilute solutions.

With the neutralized aggregating polymer, the behaviour of the solutions in a dilution experiment varies greatly with the nature of the cation used. For short polymers with Zn as a counterion, the successive dilutions give intensities which vary linearly with concentration. Then we obtain an aggregate molecular weight which is about five times that of an isolated macromolecules. With the same chain length and Ba as a counterion the measured intensities are much larger, corresponding to an apparent aggregation number of 40. For a star this is a bit surprising, but other geometries might be able to accommodate this value. Finally with larger polymers ($M_w = 30\,000$) the extrapolation to low concentrations leads to a molecular weight around

Table I.

	PS COOH 6 000	PS COOH 30 000		
LS	6 000	35 000		
Viscosity	5 400	30 000		
GPC	5 600	30 000		
PS-Zn 6 000	PS-Ba 6 000	PS-Zn 30 000	PS-Ba 30 000	
30 000	230 000	30 000 < m < 45 000	unreliable	

30 000 for the polymer with Zn as counterion, and to an unreliable result in the case of PS-Ba 30 000, because the intensity does not vary linearly with the concentration. These results are summarized in table I.

These problems may be caused by an association-dissociation process, which could make the aggregates grow or dissolve, according to the concentration of neutralized polymer in the solution. Consequently experiments at different dilutions will observe different species. Another potential problem would be the existence of non-trivial correlations between the aggregates which may not interact like hard spheres.

Such problems are particularly bad for LS experiments, which rely on extrapolations to $c \rightarrow 0$ in order to yield single particle data. To some extent they can be avoided by working at higher q values, where distances within one object or between neighbouring ones are selected. This is achieved in Small-Angle Neutron Scattering (SANS) and in Small-Angle X ray Scattering (SAXS) experiments which are presented next.

Small-angle neutron scattering from dilute solutions.

The same objects, which are observed in a light scattering experiment, can also be seen in neutron scattering, if isotopic substitution is used to achieve the appropriate contrast. Here we use the deuterated toluene as a solvent. Then the PS chains are seen with a good contrast [14] and the contribution of the ions can be neglected because, for most of them, their scattering length are close to that of PS. In this way, we used another q window, to get information about the parameters (mass, size) of individual objects.

The experiments were performed on the instrument PACE, at LLB CEN Saclay, using sample detector distances SD between 0.8 and 4.5 m and wavelengths of 7 and 10 Å. These conditions yield spectra which cover the range

$$0.004 < q < 0.5 \text{ Å}^{-1}$$

over three windows depending on λ and SD, as shown in figure 1 where the various q ranges used are compared. With a wavelength dispersion of 10 % the flux is such that samples, with polymer concentrations below 2 %, do not give a useful signal in a reasonable acquisition time, thus we performed most of our experiments above this concentration. On the same plot the q windows used in the LS and SAXS experiments are shown. These experiments, presented latter, have been performed on the synchrotron radiation in LURE (Université Paris Sud, Orsay), on the D22 apparatus. Two distances, 0.5 and 1.5 m have been used together with a 1.55 Å

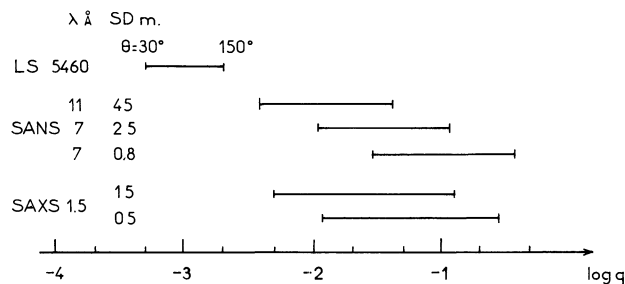


Fig. 1. — Scattering windows used, as a function of the techniques and the experimental set up.

wavelength. The same domain of scattering vector as in SANS is thus covered with a very good resolution.

A first set of experiments was performed on a 5 % solution of the various neutralized system obtained from PS-COOH 6 000. Figure 2 shows the scattered intensities obtained on PS-Ba, PS-Al, PS-Zn, PS-Mg and PS-COOH samples in a $\log I$ versus $\log q$ representation.

The acid polymer is our reference sample, and in a good solvent, it is in a random coil conformation. The Zimm approximation (c/I versus q^2 representation) on the SANS distribution, shows a linear behaviour corresponding to a radius of gyration of 29 Å. This is indeed the size expected for such a molecular weight. For the neutralized polymers the behaviour of scattered intensity is actually modified, but not in the expected way.

For the polymers neutralized with Mg and Zn the intensities are larger by a factor of 2 rather than the factor of 5 expected from the LS experiments on more diluted solutions. Moreover the radii of gyration determined through a Guinier or a Zimm representation, are lower or have the same value as that of PS-COOH. These two results are incompatible, the increase of intensity showing an increase of molecular weight while the molecular dimensions of the aggregate remain the same.

For the polymer neutralized with Al and Ba these features are even stronger. The intensities are only four times larger than those of the unassociated acid polymer, whereas the aggregation number expected from LS is of the order of 40. Also the curvature of the scattering curve results in a value close to 0 for the radius of gyration, regardless of the approximation. Obviously, these effects are caused by interferences between neighbouring scattering objects: such interferences will depress the intensities scattered at low q , and create a peak or hump at q values of the order of the inverse correlation distance.

These interparticle effects show up more clearly, with the longer polymers, where the 5 % solution of the PS-Ba 30 000 shows a peak at a correlation distance near 300 Å, which remains as a shoulder for

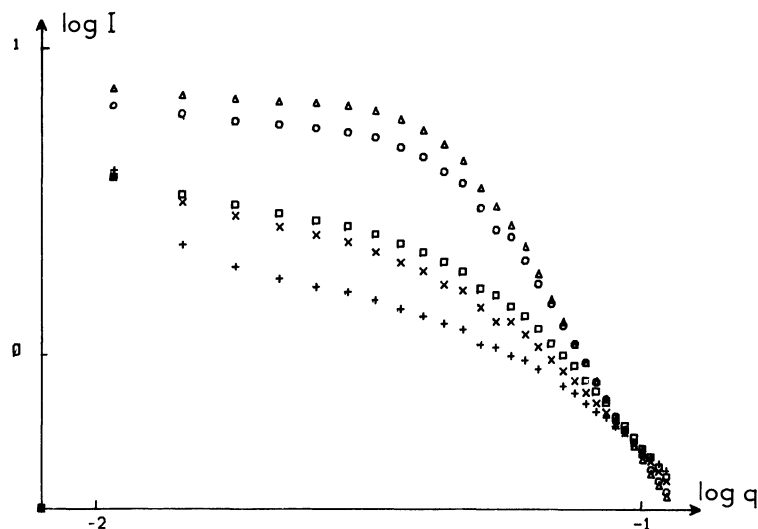


Fig. 2. — Small angle Neutron scattering intensity for 5 % solution in deuterated toluene ; (+) PS-COOH 6 000, (X) PS-Mg 6 000, (□) PS-Zn 6 000, (○) PS-Al 6 000, (Δ) PS-Ba 6 000.

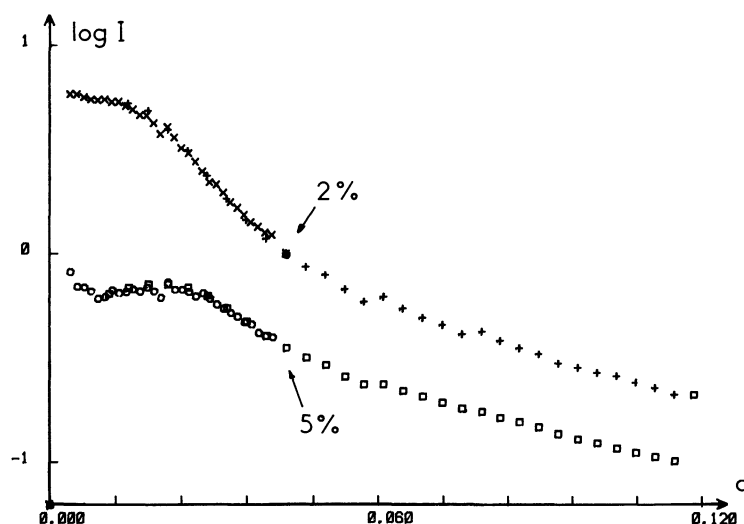


Fig. 3. — Small angle neutron scattering intensity for a 2 % and 5 % solution of the PS-Ba 30 000, for two scattering windows.

the 2 % concentration and disappears in less concentrated solutions (Fig. 3). In this figure the relative intensities have been adjusted to avoid overlap of the curves. Each solution has been studied in two q windows, and both sets of data match perfectly in the overlap region.

These results are really important ; they show that, even at low concentrations, (five times less than the estimated c^*), a strong contribution of the intercorrelation term still modifies the scattering distribution function. This could be an explanation for the incoherent results obtained through LS.

On the one hand, the existence of such strong intercorrelation effects implies that the neutralized chains are aggregated. This aggregation must depend

on the type of counterion used for the neutralization, this is evident from the change in the peak intensity. On the other hand, these effects make it impossible to extract single object parameters from the scattering curves.

Concentrated solution study using SANS and SAXS.

At this point we have to revise our goal. Because of the interferences between distinct aggregates, we cannot obtain directly the structure of the individual aggregates. However the study of these interferences gives access to the organisation of the aggregates in the sample. In turn, from the way in which their packing depends on their number density, we can

extract information on their shapes and sizes and therefore on the symmetry of the aggregation process.

The conditions for this study should be particularly favourable. If we want to study the intercorrelation term, we might as well use concentrated solutions, where this term will dominate the scattering. Then SAXS is a particularly well suited technique. Indeed when dealing with semi-dilute or concentrated solutions, the polymeric parts of neighbouring aggregates are close together or even interpenetrate each other. In such cases the intercorrelation of these chains is not simply related to the relative location of the aggregates. Therefore it is necessary to enhance the contribution from the ionic clusters and to lower that of the polymeric shells. In this respect, it is important to note that X rays are scattered by electron clouds, therefore SAXS is much more sensitive to heavy atoms and will be mainly scattered by the ionic clusters. The opposite is true of light scattering, where the contrast is dominated by the difference in the index of refraction between PS and toluene, and also of SANS where the use of deuterated toluene provides a good contrast to the protonated chains, so that the whole aggregate is observed. By this way, even in the limit of very high concentrations, or in the pure solid, where the polymeric shells of neighbouring aggregates no longer provide any contrast, the SAXS should still yield the intercorrelation between the aggregates cationic core.

The experimental evidence which supports these arguments is presented in figure 4. Here the same solid PS-Ba 6 000 sample is studied by SANS and SAXS. Neutrons yield a flat scattering curve which

contribution of the PS matrix. If there is a contribution from the weak contrast between PS and Ba, it is overwhelmed by the first two terms. X-rays show a definite peak arising from the intercorrelation between the cationic core of the neighbouring aggregates, and also an increase of the intensity toward small q values, which may be produced by a long range correlation between the cations of one aggregate.

The peak corresponds to a correlation distance around 50 Å, obtained using the Bragg law and the small-angle rise of intensity, treated in the Guinier approximation, to a radius of gyration of the order of 36 Å.

At lower concentrations a peak shows up in the SANS as well as in the SAXS curve, the comparison between both would be of interest. Figure 5 shows the scattering curves obtained through both techniques on a 5 % solution of PS-Ba 30 000 and on a 35 % solution of PS-Ba 6 000. For each sample we have scaled the intensity in such a way that the maxima obtained with both techniques will be at the same height, or, if the maxima are mere bumps, in such a way that the high q tails will match.

There are two remarkable features in this comparison :

- the location in q of the maxima are exactly the same in X-ray and neutron scattering curves ; and
- the SAXS distribution exhibits a small-angle increase of the intensity, whereas SANS does not.

The first point implies that both techniques observe the same correlation between neighbouring aggregates, even though in one case the waves are scattered by the whole object and in the other case by the cationic core only. Therefore the cores reflects properly the structure of the objects in the

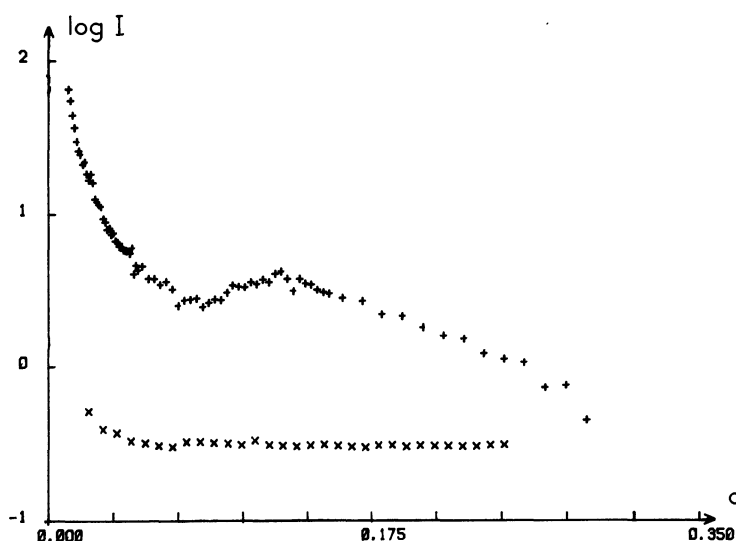


Fig. 4. — (x) neutron and (+) X ray scattering distribution for a solid PS-Ba 6 000 sample.

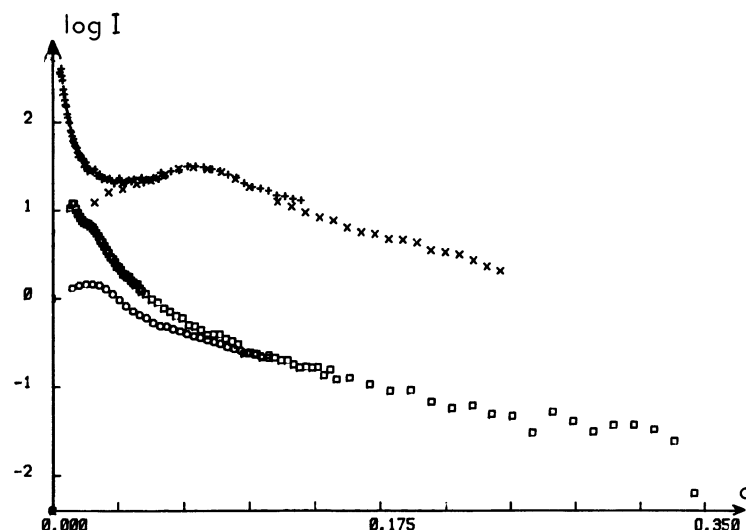


Fig. 5. — Small angle neutron and X ray scattering intensity for : (+), (x) 35 % solution of the PS-Ba 6 000 and (□), (○) 5 % solution of the PS-Ba 30 000.

solution. The second point might be caused by a long-range correlation at the core level which would contribute to the SAXS but not to the SANS and thus is necessarily related to the ionic core of the object. According to the PS-Ba 6 000 scattering curve, the correlation distance between neighbouring aggregates is of the order of 80 Å, and the radius of gyration for the long-range correlation 400 Å. These values are not compatible with a starlike model. Indeed the distance between two aggregates being less than the radius of gyration of that aggregate, a centrosymmetrical object cannot fit with these values.

However the indetermination on the structure could be solved. Important information on the structure is provided by the law for the variation of

the peak position, q_{\max} , with the concentration of the solution. Indeed, a three-dimensional packing of globular objects should give distances which vary as the cube root of concentration, for a 2-dimensional packing of rods, the law should be the square root of concentration and for a one-dimensional stacking of lamellae it should be linear with concentration. Such laws have been observed in the appropriate ranges of concentrations for amphiphilic systems [15].

Then we have determined these laws for three systems, PS-Ba 6 000, PS-Al 6 000 and PS-Ba 30 000. The q windows used have been chosen to allow the best determination of q_{\max} . However for low concentrations, precision remains poor due to a lack of resolution in SANS or to the small-angle increase of intensity in X-ray experiments. Never-

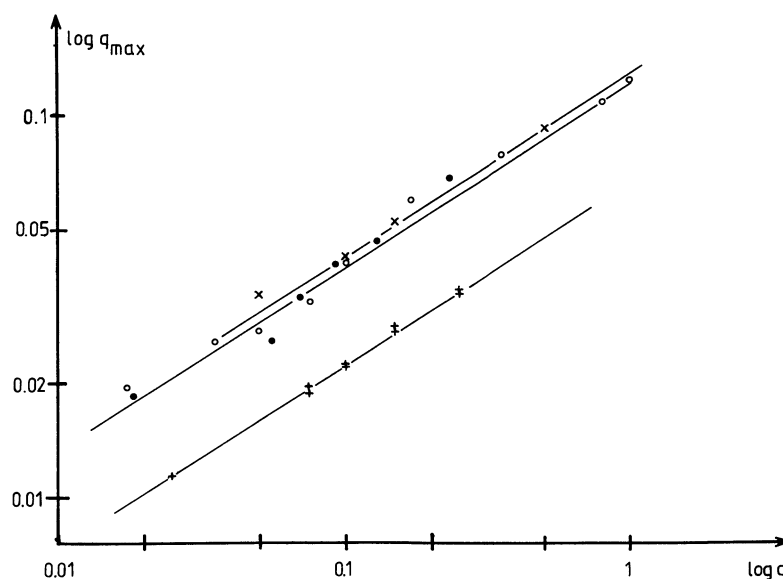


Fig. 6. — q_{\max} variation *versus* concentration for : (+) PS-Ba 30 000, (x) PS-Al 6 000 and (●), (○) PS-Ba 6 000.

theless it has been possible for the three samples to get the q_{\max} dependence over a large range of concentration. Figure 6 shows the results obtained in a $\log q_{\max}$ versus $\log c$ representation. For each sample a linear behaviour is obtained with the same slope of 0.48 ± 0.03 .

This value for the exponent is close to the square root law expected for a two-dimensional stacking of rods or cylinder and seems to indicate that, over the range of concentrations studied, we have a cylindrical structure between the object and that a cylindrical aggregation of the polymer chain occur in the neutralization process. This result is concordant with the numerical value we got for the radius of gyration and the distances from figure 4.

Since the scattering curves only show one maximum, this organisation of the cylinders must be short-range only. This may indicate that their conformations are not fully stretched but somewhat coiled-

curved. Indeed, similar scattering functions are obtained from semi-dilute solutions of linear polyelectrolytes [16]. If this analogy is meaningful, the cationic cores of our cylinders play the role of the polyelectrolyte backbone, while the electrostatic repulsions between these backbones are replaced here by the steric repulsions between the polystyrene chains which define the lateral size of a cylinder.

For the PS-Ba 30 000 the peak positions are obtained from SANS experiments only. Indeed in SAXS the small-angle intensity rise tends to sweep the peak position toward small angles when both contributions are in same q domain. With SANS, the peak disappears progressively at concentrations in excess of 25 %, this indicates an overlap of the PS chains from neighbouring cylinders, or at least a uniform distribution of the scatterers through the sample, but not a loss of the order. This interpretation is confirmed by the SAXS results, for which

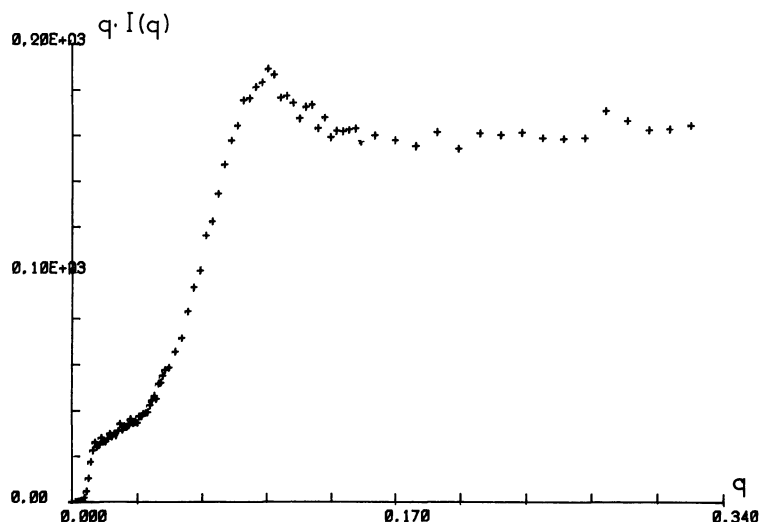


Fig. 7. — $qI(q)$ versus q representation for the PS-Al 6 000, 50 % solution.

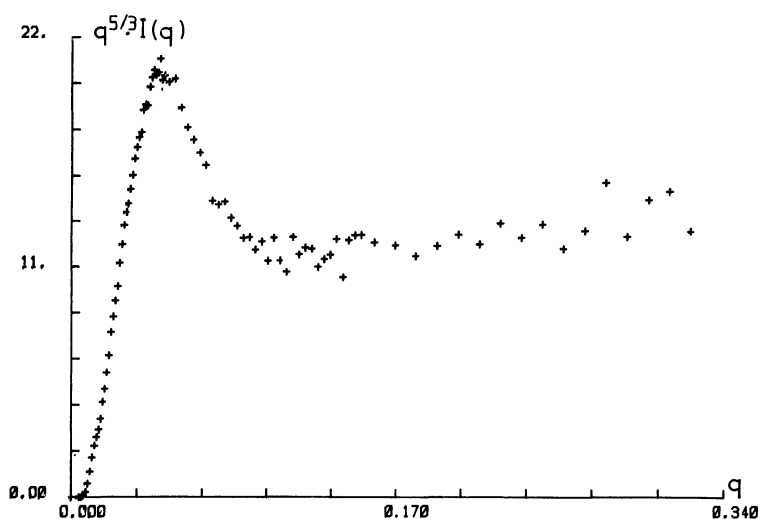


Fig. 8. — $q^{5/3}I(q)$ versus q plot for the PS-Ba 6 000, 5 % solution in toluene.

the maximum is still obtained over this range of concentrations, but moreover give a multiple peak distribution function [16] for higher concentrations.

The variation obtained with the PS-Al samples is very close from that of PS-Ba 6 000, whereas those of PS-Ba 30 000 yield much smaller values of q ; this difference may be easily justified. Indeed in the latest case the molecular weight of the chain is much larger, thus they are more bulky and require a larger distance between cylinders and then lower value of q_{\max} . For the PS-Al 6 000, the q_{\max} values are slightly higher than for PS-Ba 6 000, this difference is significant, and it may be correlated with the smaller intensity obtained in SANS experiments for PS-Al (Fig. 2). Indeed at a given overall concentration of chains, a relatively smaller intensity indicates that the density of scattering chains in a cylinder is lower, i.e. the number of branches per unit length of cylinder is lower. This will translate into a higher number of cylinders per unit volume hence shorter distances between them and a higher value of q_{\max} . The case of polymers with Zn, Mg or K counterions is less clear, since the q_{\max} values are smaller while the intensity is also lower (Fig. 2), since for these polymers we have data at one concentration only (20 %) we cannot draw any conclusion on their behaviour.

The cylinder model for the aggregates is supported by another argument which derives from the asymptotic range of the scattering curve. In this range the interferences between neighbouring aggregates have decayed and the SAXS intensity should reveal the conformation of the ionic core. Figures 7 and 8 show two typical results. For the PS-Al 6 000 at a concentration of 50 % the plot of $q \times I(q)$ shows a well defined plateau which matches the $1/q$ behaviour expected for a rigid rod. For the PS-Ba 6 000 at a concentration of 5 %, the plateau is obtained in a plot of $q^{5/3} I(q)$; this is the behaviour expected for a flexible polymer with excluded volume. A

straightforward interpretation of these two results would be that the ionic cores behave as flexible polymers at low concentrations because the range of their steric repulsions is short as compared to their distances, while at high concentrations they behave as rigid rods the range of their steric repulsion being of the order of their distances. This point needs to be confirmed through more systematic experiments.

Conclusion.

This first set of results shows that the monoionic polymers do not behave as we previously thought. For the neutralized polymers, an aggregation of the ionic groups occurs, which varies according to the polymer molecular weight, the type of counterion and the concentration of the solution. The symmetry of the aggregates is not, as we first believed, spherical, but rather cylindrical in most of the concentration range. We have also found evidence for a lamellar organisation, this result will be presented in a subsequent paper [16].

More systematic experiments are needed to complete the description of these systems, they would certainly allow a better understanding of their relation to halatotelechelic polymers and, more generally, to ionomers.

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