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Analysis

Small-Angle X-Ray Scattering Study of Halato-Telechelic Polybutadienes

J. Ledent[1], F. Fontaine[1*], H. Reynaers[2], and R. Jerome[3]

[1] Laboratory of Experimental Physics, University of Liege, Sart Tilman, B-4000 Liege, Belgium

[2] Department of Chemistry, University of Leuven, Celestijnenlaan 200 F,
B-3030 Leuven-Heverlee, Belgium

[3] Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liege,
Sart Tilman, B-4000 Liege, Belgium

SUMMARY

The small-angle X-ray scattering curves of carboxy-telechelic polymers exhibit very strong scattering at the lowest angles which points to the presence of large aggregates in the samples. Beyond the position of the main scattering maximum, common to all ionomers, a faint modulation is observed at a position corresponding to a second diffraction order. These observations are discussed with respect to other data in the litterature.

INTRODUCTION

Despite extensive studies carried out on ionomers, the important question of their microstructure remains unanswered. The existence of ionic aggregates is generally recognized, but their nature is still not clear: the problem of their shape, size, internal structure and distribution in the polymeric material is not solved.

A considerable research effort has been expended to elucidate the morphology of ionomers. Small-angle X-ray scattering constitutes a basic technique in this field. Simultaneously with SAXS, however, other techniques have been exploited: SANS, electron microscopy, electron paramagnetic resonance, Mössbauer spectroscopy...

The SAXS patterns generally exhibit a well defined peak, often called ionic peak, corresponding to a Bragg spacing "d" of a few nanometers. It is important to note that this peak is typical for the neutralized form of the polymer and generally does not occur in the acid form. It is the earliest and most direct evidence for the existence of some kind of ionic aggregation in ionomers.

Two approaches have been followed to explain the ionic scattering maximum and the other SAXS features. The main characteristic of the first approach is to attribute the ionic peak to an interparticle interference. Various qualitative models have been suggested to support this point of view (1-6). In the second approach, other qualitative models have been proposed wich relate the peak and eventually other SAXS features to an intraparticle interference due to the internal structure of the ionic aggregates (7), (8), (4).

A quantitative analysis of such models has been performed (9). The fitting of the calculated SAXS curves to the experimental data is not entirely satisfactory. Other attempts have been made to build quantitative models (7,9-12). In spite of all these efforts, the basic problem of the morphology of ionomers remains a matter of uncertainty.

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[*] To whom offprint requests should be sent

Most of the studies in the past have been devoted to polymers composed of a hydrocarbon backbone carrying randomly distributed acid groups, neutralized to form salts. A major improvement in these studies has been the introduction of halato-telechelic polymers obtained by neutralization of carboxy-telechelic polymers. These are "model" compounds thanks to the large control applicable to the prepolymer length and ion content and to the nature of both the backbone and cation as it has been pointed out by Broze et al. (13). These authors, using a Guinier-type camera, observed two diffraction orders with Bragg's spacings in the ratio 1:2, an observation which has been ascribed to a lamellar organisation of the material. Such a morphology is consistent with their finding that a linear increase in thickness "d" of the lamellae is observed with increasing molecular weight, i.e. length of the polybutadiene backbone.

The observation of a second diffraction peak contrasts with all other works. As a consequence it was decided to repeat some of these measurements with a Kratky-camera which in the small-angle region is superior to the Guinier-camera.

EXPERIMENTAL

The halato-telechelic polymers (HTP) were prepared from carboxy-telechelic polybutadiene (PBD) commercialized by Goodrich. Its microstructure consists of 80 % 1,2 and 20 % 1,4 units and $\bar{M}_w/\bar{M}_n = 1.8$. HTP were obtained by adding stoichiometric amounts of metal methoxide (freshly prepared in methanol at ca. 5 %) to carboxy-telechelic polybutadiene in dry toluene. The methanol formed was distilled off under reduced pressure to displace the reaction equilibrium completely. The following equation exemplifies the neutralization:

$$n\ \mathrm{HOOC{-}P_x{-}COOH} + n\ \mathrm{Me^{++}} \rightarrow \left[{}^{-}\mathrm{OOC{-}P_x{-}COO^{-}\ {-}Me^{++}} \right]_n$$

In this work Ba^{++} -, Mg^{++}- and K^{+}-derivatives have been prepared. Samples were dried under vacuum down to constant weight and pressed between micaplates in the sample holder. Sample thickness was approximately 0.9 mm (Ba^{++}-and Mg^{++}- samples) and 1.8 mm (K^{+}-sample).

The very weak small-angle X-ray scattering of the samples was registered by a Kratky compact camera mounted directly on the tube shield of a stabilized Philips X-ray generator. Cu $K\alpha$ radiation was used throughout. The scattered intensity was registered with a Xe-filled proportional counter. Monochromatization was simulated by a Ni β-filter in conjunction with a pulse height discriminator. With respect to the classical Kratky system, a major advantage of the compact camera is the fact that the sample is mounted in a heating stage within the evacuated camera, considerably reducing air scattering. All measurements were made by a step scanning procedure and in the fixed time mode, with a sampling time of 300 secs for each step. The entrance and detector slits were mostly adjusted to 100 and 250 μ respectively, corresponding to an ideal resolution for the camera of 800 Å, as claimed by the manufacturer.

The system was used in the finite slit approach. Corrections were made for the slit smearing effect using the desmearing procedure of the FFSAXS4 program (14).

RESULTS AND DISCUSSION

Figure 1 exhibits the SAXS-patterns observed on our samples of Mg^{++}-, Ba^{++} - and K^{+}-carboxylatopolybutadiene. These data were obtained at room temperature. The three curves show the same general appearance and can be divided in three parts.

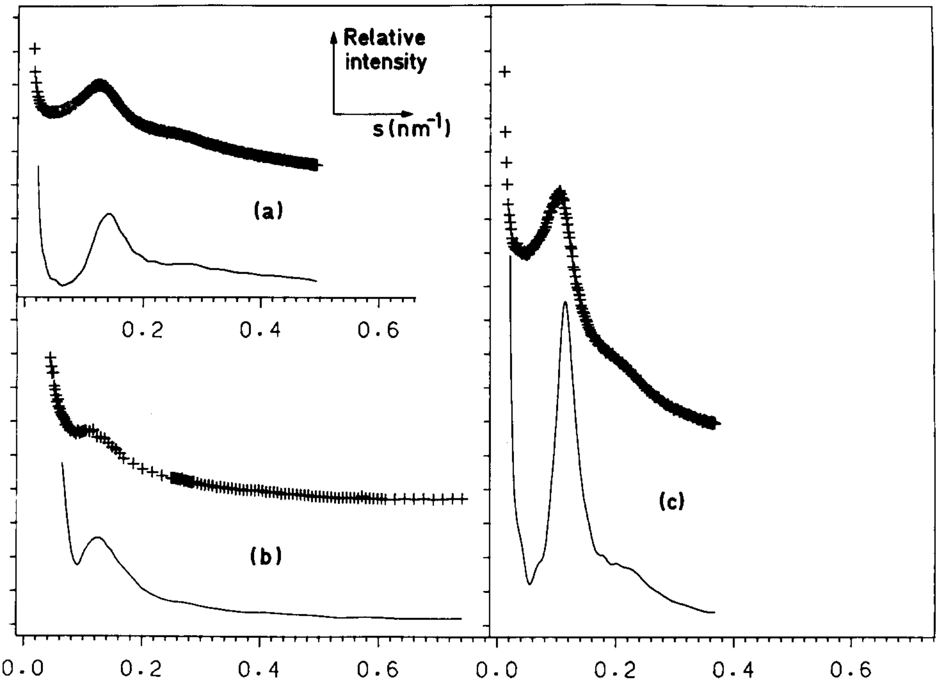

Figure 1 - SAXS-patterns of Ba^{++}(a)-, Mg^{++} (b)- and K^{+} (c)-carboxylatopolybutadiene at room temperature. (+++ observed data, —— desmeared data).

1.- At very low angles an upswing in intensity is always observed towards the zero scattering angle clearly before the influence of the primary beam can interfere: the intensity of the latter indeed, rapidly increases as its edge is approached. Anyhow removing of this background is generally done by registration and substraction of the blank scattering. Other reasons proper to the sample and sample preparation can also contribute to the scattering at the lowest angles, these include the presence of large aggregates and impurities as well as void scattering.

Figure 2 shows after substraction of the blank scattering the resulting Mg^{++}-curve for the lowest s-values.

It clearly appears from this figure that the existence and importance of the upswing in intensity towards the origin is significant and suggests the presence of large aggregates.

2.- The other end of the SAXS pattern is the so called tail of the scattering curve. According to Porod's law (15) the intensity in the tail of the scattering curve of a two-phase structure shows a s^{-3} behaviour for smeared data (s^{-4} for desmeared data).
More explicitely

$$\lim_{s\to\infty} \left[s^4 . I(s)\right] = \frac{2}{\pi} \lim_{s\to\infty} \left[s^3 . \tilde{I}(s)\right] = K$$

In this equation, s stands for $(2 \cdot \sin\Theta)/\lambda$, $\underset{\sim}{\tilde{I}}(s)$ for the measured (smeared) intensity, I(s) for the pinhole (desmeared) intensity and K is a constant.

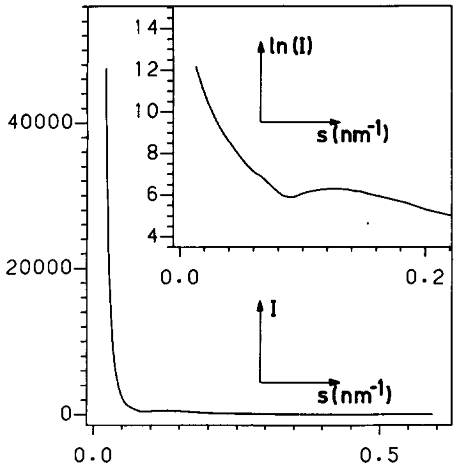

Figure 2 - Scattering curve for Mg^{++}- PBD (a). Plot of ln I versus s for data at the lowest angles in insert (b). All data after substraction of blank scattering.

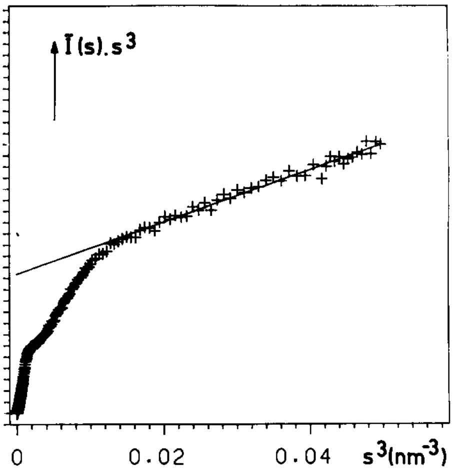

Figure 3 - POROD asymptotic tail behaviour of the relative scattering intensities. Plot of $s^3.\tilde{I}(s)$ versus s^3 : K^+-sample.

Porod's law is valid as long as there is a well defined sharp phase boundary between two homogeneous phases. In practice, Porod's law works fairly well in dense semi-crystalline polymer systems with a high degree of crystallinity as, for instance, the linear high density polyethylene.

Including an s-independent term for the background of the intensity, Porod's rule can be written:

$$\tilde{I}(s) = K_1\, s^3 + K_2.$$

Here K_1 is the so-called Porod's constant. Multiplying the above equation by s^3 , one gets:

$$s^3.\tilde{I}(s) = K_1 + K_2\, s^3.$$

Thus, a plot of $s^3.\tilde{I}(s)$ versus s^3 gives in the case of a two-phase system a straight line with slope K_2 which is a measure of the background. This plot applied to the Mg^{++}-, Ba^{++}- and K^+-PBD effectively leads to a straight line as can be seen from figure 3 for the K^+-sample.

As a consequence of the low scattering power of the samples and the slow decay in the tail of the curve the registration in some cases has been interrupted before $\tilde{I}(s)$ had dropped to zero. In such a case the pinhole curve as given by Vonk's desmearing procedure would present at its right-hand side a factitious "upswing" as a compensation for the failing intensity values beyond the observed region. Vonk's procedure has thus been adapted (16) so as to include in the unknowns of the problem that determine the pinhole curve searched for, a small number of additional unknowns (maximum five; two in this work) to fix the boundary conditions towards the wide angles i.e. force the desmeared curve to continue beyond the observed region in a way consistent with Porod's law in s^{-4}.

3.- The most pronounced feature in the scattering curves is the single maximum, which has been observed by all other investigators for ionomers of different chemical nature. By simple application of Bragg's law to this maximum, a spacing "d" is obtained (see table 1), the nature of

Table 1. Bragg's spacing of several salts of carboxy-telechelic polybutadiene at room temperature.

cation	d(nm)			
	This work	Broze et al. (13)	Williams et al. (19)	Average values
Mg^{++}	7.7	6.9	6.3	7.0 ± 0.7
Ba^{++}	7.2	7.1	7.5	7.3 ± 0.2
K^{+}	8.7		7.2	8.0 ± 0.8

which is until now unclear. Table I compares the values of "d" reported elsewhere for samples of the same chemical composition but prepared independently of each other. Except for Ba^{++} , a significant discrepancy is reported for Mg^{++} and K^{+} which could stress the dependence of the morphological details on the sample history (i.e. differences in the molding, storing and ageing conditions).

There is no distinct observed second order diffraction peak (17) although, chiefly in the case of the Ba^{++} - and K^{+} -compounds, a fair shoulder or some oscillations can be seen as well on the observed as desmeared curves (figure 4) in the region where a lamellar structure would produce a second order maximum.

Table 2. Positions in nm of the main (I) and the possible second order diffraction peak (II) of several metal carboxylato-telechelic polybutadiene at room temperature.

cation	I	II	ratio
Mg^{++}	7.69	3.67	2.1
Ba^{++}	7.18	3.58	2.0
K^{+}	8.66	4.43	1.95

If these modulations are significant of the existence of a second order diffraction peak, it arises less from their magnitude which is actually very weak, than from their systematic position in a ratio 1:2 with respect to the well defined peak (Table 2).

As a consequence of the weak scattering power, Williams et al. (18),

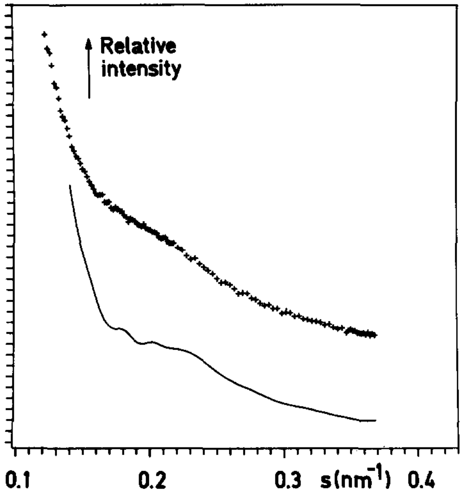

Figure 4 - Detail of scattering curve of K^{+}-PBD, exhibiting a shoulder at the position of an eventual second order maximum.

+++ observed data

—— desmeared data

(19) used synchrotron radiation on identical samples in order to obtain more details in the registration of the scattering patterns. These synchrotron results give no evidence for a second order maximum either.

It is tempting to use Guinier's law to calculate a radius of gyration in order to assess the dimensions of the domains containing the aggregates of cations. According to Guinier (20), for a dilute system of uniform particles and at the very low angles, the scattering intensity may be written to a good approximation as

$$I(s) = I(0)\ \exp(-4/3\ \pi^2 s^2 Rg^2)$$

Hence, by plotting $\log_e I(s)$ versus s^2, a radius of gyration Rg can be calculated from the slope of the linear part of the plot towards the zero angle. Such a kind of analysis, using the Guinier treatment or related methods, has been made, although with some restrictions, on ionomers by authors as Macknight et al. (7), (15), Pineri et al.(5), Moudden et al. (4), Meyer et al. (8), Roche et al. (21), Peiffer et al. (6). It is not completely clear if this procedure can be justified due to the presence of the main maximum in the linear part of the Guinier plot. However, doing so, values of 0.61, 0.46 and 1.16 nm are obtained for the Rg of respectively Mg^{++}-, Ba^{++}- and K^{+}-carboxy-telechelic PBD at room temperature, values which are comparable to the ones given for various ionomers by the previously cited authors.

The applicability of Guinier's approximation to our samples and the significance of the size parameter so obtained remain questionable. Indeed, it must be emphasised that the mean scattering peak indicates an interference phenomenon and that the scattered intensity strongly increases towards the lowest angles as stated above. This upswinging part of the curve appears to be tangent to a straight line which should give a very large value of Rg (35 nm or more).

The examination of the scattering patterns obtained with increasing temperature points to the rather rigid nature of the network structure of the samples (17). It can be clearly seen from figure 5 that the position of the scattering maximum is insensitive to temperature, for the Ba^{++}-sample, within the range from 25°C up to 140°C. The same observation is made for the Mg^{++} - sample within the range from 25°C up to 100°C. The K^{+}- carboxy-telechelic PBD exhibits a spacing of 8.7 nm which decreases systematically to 7.8 nm with increasing temperature up to 80°C.

The modulations in the second order region persist in the curves at higher temperatures at least for the Ba^{++}- and K^{+}-compounds.

These experimental results support a difference in the thermal stability of the ionic aggregates formed by alkaline and alkaline-earth carboxylates, respectively. This conclusion is in agreement with measurements of thermally stimulated depolarization currents which exhibit a dramatic increase in the intensity of the ρ peak (ionic migration) when alkaline cations are substituted for alkaline-earth cations (22). It would mean that the thermal dissociation of the ionic aggregates occurs easily for alkaline carboxylates in comparison with alkaline-earth carboxylates.

CONCLUSIONS

The morphology of carboxy-telechelic polymers has been explored by small-angle X-ray scattering. Starting from samples with well-defined molecular weight, Ba^{++}-, Mg^{++}- and K^{+}-derivatives have been prepared.

These samples all exhibit spacings between 8.7 and 7.0 nm at room and higher temperatures. The origin of this spacing remains unclear. The position of the scattering maximum is rather temperature-independent

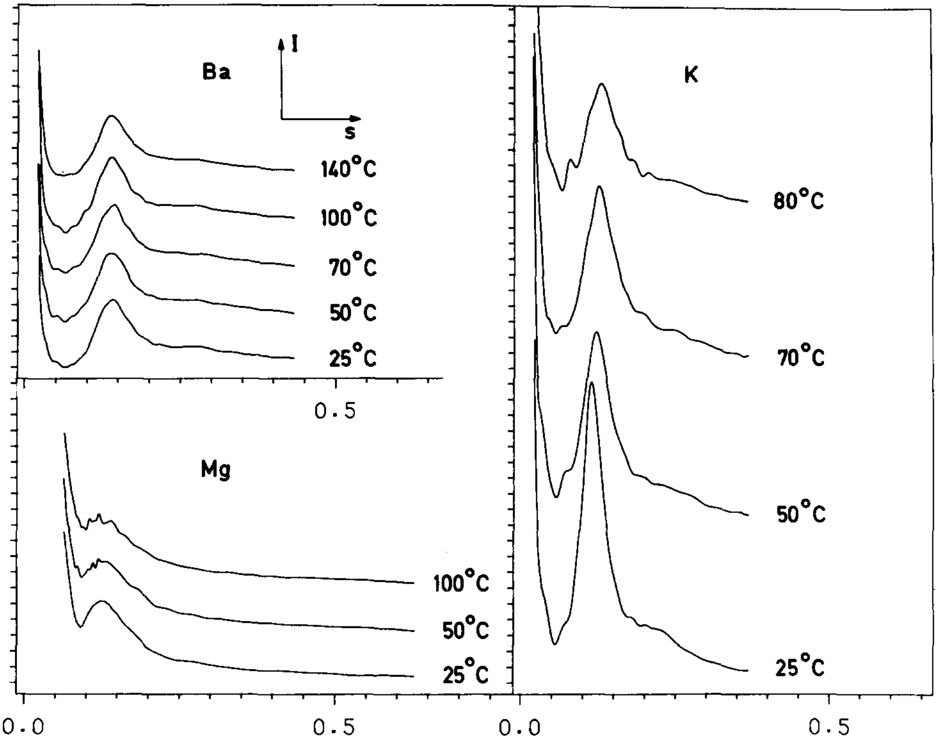

Figure 5 - Temperature dependence of scattering curves. Samples as in figure 1.

pointing to the rigidity of the network structure of the samples.

Significant very strong scattering is observed at the lowest angles. The asymptotic behavior of the tail end of the scattering curve indicates, in agreement with Porod's law, a two-phase nature of the system.

It remains hazardous to try to obtain a radius of gyration from the Guinier approximation.

Because of the absence of an evident second diffraction order, the previously proposed lamellar structure remains tentative.

The present experimental evidence is not sufficient to define in a unique way the morphology of these carboxy-telechelic polymers. Further experiments are needed. At least scattering curves must be measured on samples with different lengths of the polybutadiene backbone, for a greater variety of cations, for samples swollen with solvents or saturated with water, etc... in order to clarify the main features observed in our scattering curves, i.e. the significant strong scattering at the lowest angles and the presence of a faint modulation in the curves beyond the ionic peak. It is clear that any model calculation should account for these observations.

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