Communications to the Editor

Small-Angle X-ray Scattering Study of Carboxylato-Telechelic Poly(*tert*-butyl acrylate)s

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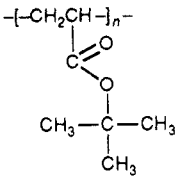
Introduction. Ionomers have been the subject of numerous studies for many years, due to their unique set of mechanical and rheological properties. Although it is accepted that the mutual association of the 10–15 mol % of ionic groups attached to a hydrophobic polymer chain promotes the thermoreversible cross-linking and reinforcement of the base polymer, the understanding of the relationship between the complex properties of ionomers and their microstructure is still unclear. Halato-telechelic polymers (HTP) have been designed as model ionomers or model networks. The ionic groups are selectively located at the chain ends, instead of being randomly distributed along the chain as with the ionomers. As a result, molecular characteristics are well-defined; they can be varied as desired, and the formation of a regular network is expected from the association of the ionic end groups.[1]

The first theoretical attempt to approach the morphology of ionomers is that of Eisenberg,[2] which relies upon the contact ion pair as the basic structural entity. Steric arguments and energetic considerations suggest that ion pairs tend to associate into multiplets and that clusters result from a loose association of multiplets. The multiplet-cluster model has been recently revised by Eisenberg et al.[3] Whatever their intimate structure, the ionic aggregates are the most characteristic morphological feature of ionomers and HTP's.

A great deal of investigations have been devoted to the microstructure of ionomers and HTP's. Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) have provided the most convincing evidence of microphase separation. A well-defined peak in the SAXS profile is usually observed and designated as the "ionic peak". The peak position corresponds to a Bragg spacing of a few nanometers (2–10 nm) for both HTP's[4,5] and ionomers.[6–8] The ionic peak is the signature of a microphase separation promoted by a large difference in polarity between the salt groups and the hydrophobic polymer matrix. Although the ionic aggregates are the basic scattering units, it is not clear yet whether the scattering results from intraparticle interference or from interparticle interference. Furthermore, the various models that have been proposed to describe the microstructure of ionomers do not properly fit the whole q-range of the SAXS pattern,[9–12] where the scattering vector $q = 2\pi s$ and $s = 2 \sin \theta/\lambda$; θ is half the scattering angle, and λ is the wavelength of the incident X-ray beam. Models are usually unable to fit the zero-angle scattering region where an important upturn in intensity is observed. This increase in intensity is another characteristic feature[4,5,9–13] of the SAXS patterns of ionomers and HTP's, the origin of which is not yet known. Nevertheless, according to several authors,[14–18] the upturn could be related to the spatial organization of the ions.

This paper reports preliminary SAXS data on a novel class of HTP's based on a polyacrylate backbone, the cross-sectional area of which is definitely larger than the cross-sectional area of the metal carboxylate end groups. Poly(*tert*-butyl acrylate) (PtBA) has been selected for a segmental cross-sectional area which is approximately 6.6 and 2.5 times larger compared to the previously studied polydienes, i.e., polybutadiene-1,4 and polyisoprene-3,4, respectively.[4,5,19] Moreover, the size of the metal carboxylates is ca. 30 times smaller than the chain cross-sectional area.



Experimental Section. Materials and SAXS Measurements. α,ω-Dicarboxypoly(*tert*-butyl acrylate) was prepared by living anionic polymerization of *tert*-butyl acrylate,[20] followed by deactivation with CO_2. A PtBA sample with $\bar{M}_n = 22\,000$, $\bar{M}_w/\bar{M}_n = 1.2$, and functionality = 1.9 was used in this study. It was quantitatively neutralized in toluene under anhydrous conditions by using stoichiometric amounts of highly reactive sodium, magnesium, and barium methanolate, respectively.[1]

SAXS intensities were measured with a Kratky compact camera and a classical stabilized X-ray generator. Cu Kα radiation was used. Details on the experimental device and the measurement procedure were reported elsewhere.[21,22] Three hundred steps were used in the step-scanning procedure, and the first 100 steps were performed with a stepping interval of 20 μm in such a way that they covered the $0.006 \leq s \leq 0.07$ nm^{-1} range. The scattered intensity was measured in the fixed time mode with a sampling time of 200 s/step. Nevertheless, on the low s-side, the intensity was high enough to allow the fixed count mode to be used at rate of 100 000 counts/step. Absorption, sample thickness, parasitic scattering, and electronic noise were taken into account in the standard manner.[21]

Desmearing Processing. Data were collected in the finite-slit mode, and the slit-smearing effect was corrected by using both the FFSAXS4 program by Vonk[23,24] and an original method reported by Sobry et al.[22] The latter relies upon the fact that the smeared intensity at a position s_1 only depends on the pinhole intensity at $s \geq s_1$. Thus, the pinhole intensity $\mathbf{I}(s_1)$ at s_1 only depends on the smeared intensity $\tilde{I}(s_1)$ and the pinhole intensity at points that lie

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Table I
Relative Position of the Scattering Peaks Observed for Metal α,ω-Dicarboxylatopoly(*tert*-butyl acrylate) ($\bar{M}_n$ = 22 000) in the Low *s* Region

Bragg spacing (nm)			*s* value (nm^{-1})			relative position			
Na	Mg	Ba	Na	Mg	Ba	Na	Mg	Ba	hexagonal lattice
71.5	65.3	67.2	0.014	0.015	0.015	1.0	1.0	1.0	1.0
46.5	39.1	45.2	0.022	0.026	0.022	1.5	1.7	1.5	1.7
35.2	29.8	34.2	0.028	0.034	0.029	2.0	2.2	2.0	2.0
27.1	23.7	25.6	0.037	0.042	0.039	2.6	2.8	2.6	2.6
	19.5	21.1		0.051	0.047		3.3	3.2	3.0
		18.6			0.054			3.6	3.5–3.6
	16.6	16.0		0.060	0.063		3.9	4.2	4
	14.8			0.068			4.4		4.4–4.6
	13.3	14.0		0.075	0.072		4.9	4.8	5.0

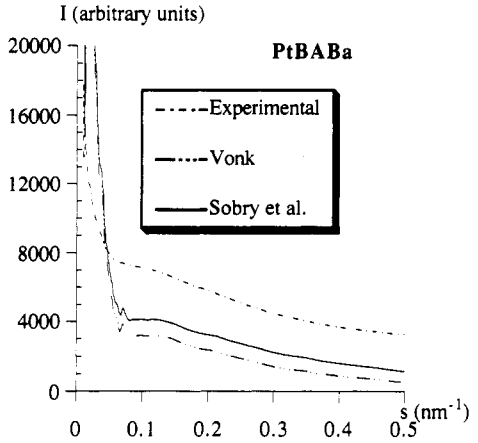

Figure 1. SAXS profiles of barium α,ω-dicarboxylatopoly(*tert*-butyl acrylate) ($\bar{M}_n$ = 22 000) on a large *s* range.

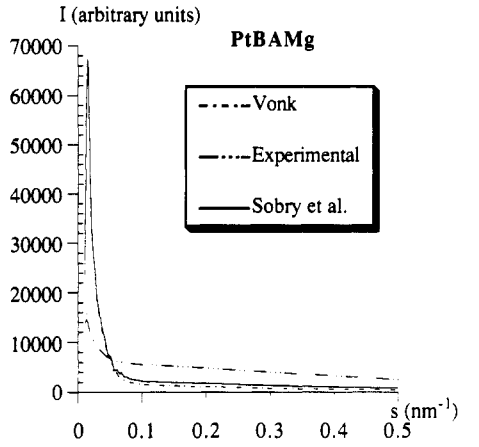

Figure 2. SAXS profiles of magnesium α,ω-dicarboxylatopoly(*tert*-butyl acrylate) ($\bar{M}_n$ = 22 000) on a large *s* range.

beyond s_1. So, $\mathbf{I}(s_1)$ can be calculated from an analytical expression of $I(s)$ at the end of the curve ($s > s_1$). Then, going back toward the beginning of the curve in a stepwise manner allows the pinhole intensity to be calculated at each point for which the smeared intensity has been measured. An analytical expression for $I(s)$ at large *s* values, in the small-angle domain, results from Porod's analysis combined with an appropriate background subtraction. An original method of background subtraction has been used which takes account of the Porod term in the background evaluation.[22]

Results and Discussion. Very surprisingly, the traditional "ionic peak" goes undetected in the SAXS profile of the α,ω-dicarboxypoly(*tert*-butyl acrylate) associated with Ba, Mg, and Na, respectively. This is in sharp contrast to all the other α,ω-metal carboxylate polydienes and poly(vinyl aromatics) which have been investigated so far.[4,5,25-27] A careful examination of Figure 1, however, shows a slight modulation in the SAXS profile of the Ba-containing sample. The faint maximum is observed at a Bragg spacing of ca. 8.4 nm, i.e., a distance that corresponds to the end-to-end distance of the PtBA chain as calculated from the characteristic flexibility of that polymer. It is worth recalling here that the Bragg spacing of α,ω-sulfonatopolyisoprene has been found to increase from 5.9 to 10.8 nm when $\bar{M}_n$ changes from 5500 to 10 000.[25] The apparent, although very weak, "ionic peak" is no longer detected when Mg (Figure 2) and Na are used as a counterion, respectively. The diffusion of ionic aggregates with the alkaline earth Mg as the cation is weaker than that with Ba. This could explain the disappearance of the residue of the ionic peak with Mg as the counterion. Finally, no significant scattering intensity is measured at *s*-values higher than 0.15 nm^{-1} in contrast to the previously investigated HTP's.[4,5,25-27]

Figure 3 emphasizes a second original observation. A

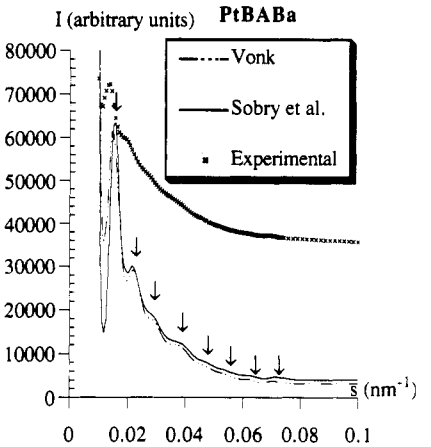

Figure 3. SAXS profiles of barium α,ω-dicarboxylatopoly(*tert*-butyl acrylate) ($\bar{M}_n$ = 22 000) in the range of low *s* values.

clearly marked series of peaks is superimposed on the strong forward scattering which is usually observed in the SAXS profile of ionomers and HTP's. Eight maxima are actually detected in a Bragg spacing range of 70–15 nm, when Ba^{2+} and Mg^{2+} are associated with the carboxylate end groups. That characteristic feature is less pronounced for the Na counterion; then only four maxima are observed. The relative positions of the maxima in the low *s* region are consistent with a hexagonal lattice as shown in Table I. The experimental SAXS patterns are independent of the desmearing methods used in this work and reproducible when the scattering measurements are repeated on independently prepared samples.

The scattering profile of Figure 3 is reminiscent of certain liquid-crystalline structures observed for aqueous solutions of amphiphiles, such as a hexagonal phase reported by Luzzati et al.[28] and supported by the relative position of six scattering maxima. It is interesting to note that a series

of five scattering peaks have been reported for short-length polyisoprene chains ($\bar{M}_n$ < 8600), selectively capped at one end by a sulfonate zwitterion.[29] These peaks have been indexed as a hexagonal lattice, although the spacing is on the order of only 10 nm.

A highly regular supramolecular structure is quite unusual in ion-containing polymers. Until now, a very simple picture has emerged from the SAXS study of all the halato-telechelic polydienes (HTPD) which have been characterized.[4,5,25-27] The distances between the ionic aggregates increases as the molecular weight between the ionic end groups is increased. At the same time, the overall organization remains unchanged and it has been proposed to consist of multiplets surrounded by a volume from which other ionic aggregates are excluded and arranged in space in a liquidlike manner. As a rule, the SAXS profile of HTPD displays a second diffraction order, the uncertainty of which has prevented the proposal of a reliable structure for the ionic aggregates. On the other hand, the SAXS patterns of the previous HTPD exhibit a very sharp contrast with those of the above presented PtBA's. First, the s^* values of the first peak are substantially different: on the order of 0.015 nm^{-1} for the PtBA's and of 0.1–0.2 nm^{-1} for the HTPD. Second, the second-order diffraction peak is seen at $1.7s^*$ for the PtBa's (see Table I) and at $2s^*$ for the HTPD. Third, a series of eight (or four) peaks is observed with the PtBA's and only one or two maximums for the HTPD.

The systematic study of the solution properties of magnesium α,ω-dicarboxylato polymers ($\bar{M}_n$ = 4000), in toluene at 25 °C, has shown that the solution goes through a sol–gel transition at a concentration which increases with the cross-sectional area of the polymer chain.[19] In this paper the question on to determine whether the ion-pair association is modified by the cross-sectional area of the polymeric backbone when the size of the ionic groups is small has been addressed. The answer to that question is yes based on the preliminary data reported in this paper. However, further investigations based on polymer backbones of various segmental cross-sectional areas should be carried out before a definitive conclusion can be reached.

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