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The structural order of some novel ionic polymers : 1. X-ray scattering studies

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SUMMARY:
   A set of novel zwitterionic side-chain polyacrylates and polymethacrylates is studied by X-ray scattering. The structural order both in the short-range and long-range scale is investigated. The influence of the polymer backbone, of different locations of the ionic groups in isomeric polymers, of bound water and of added inorganic salts on the bulk structures is studied, and the observed rearrangements are analysed.

Introduction

   One of the most interesting effects of ionic polymers with flexible chains is the formation of various structural order when the precursor polymers, e.g. bearing acid groups, are converted into salts [1-3]. Generally, the conversion to polymeric salts is accompanied by the formation of more ordered structures whose nature is not fully elucidated up to now. The situation is even more complex for polymers which show order in the non-ionic form. In such cases, the salt formation can lead to unpredictable rearrangements of the initial structure [2].

   A particularly interesting case is given for zwitterionic polymers [4,5]. In such polymers, all ions are fixed to the polymer backbone, and low-molecular-weight counterions are missing. As each macromolecule bears the same number of cationic and anionic groups, the individual macromolecules are uncharged in spite of the high concentration of ionic groups present. Nevertheless, zwitterionic polymers are potentially capable of binding both cations and anions of a low-molecular-weight salt added. Hence, with such systems homogeneous blends of equimolar mixtures of polymer and inorganic salt may be possible. This was demonstrated recently for some poly(sulfobetaine)s [6,7]. Furthermore, when modified by hydrophobic chains, the crystallization of such polymers can be suppressed, but inducing the formation of superstructures [8]. However, structural details are missing yet, and the effect of water on the structures observed is not clear.

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To elucidate the initial order and possible structural rearrangements in ionic side-chain polymers, we have studied two sets of isomeric polyzwitterions in detail. These are the isomeric polyacrylates poly{3-[*N*-(11-acryloyloxyundecyl)-*N*,*N*-dimethyl]-ammonio propanesulfonate} (**A1**) and poly{3-[*N*-(2-acryloyloxyethyl)-*N*,*N*-decylme-thyl]ammonio propanesulfonate} (**A2**) and the analogously built isomeric polymeth-acrylates poly{3-[*N*-(11-methacryloyloxyundecyl)-*N*,*N*-dimethyl]ammonio propane-sulfonate} (**M1**) and poly{3-[*N*-decyl-*N*-(2-methacryloyloxyethyl)-*N*-methyl]ammonio propanesulfonate} (**M2**)[8]. In this part we consider general features of the scattering data connected with the formation of superstructures. In part 2[9], models of molecular packing based on calculations of correlation functions and density distributions will be presented. The four polymers under investigation are shown in Scheme 1.

Scheme 1:

$$\text{A1} \qquad \text{M1} \qquad \text{A2} \qquad \text{M2}$$
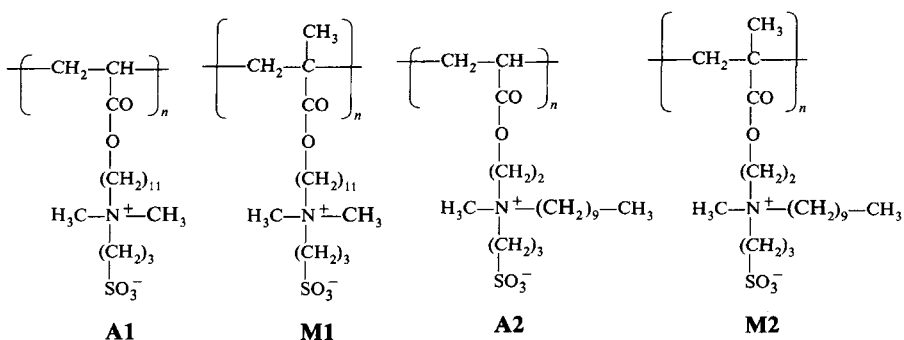
In polymers **A1** and **M1**, the ionic groups are separated from the polymer backbone by long alkyl spacers. In contrast, in polymers **A2** or **M2** the ionic groups are attached closely to the backbone. Hence the comparison of the isomers allows to investigate the influence of the location of the ionic groups. Further, the comparison of the polyacry-late series with the polymethacrylate series allows to study the influence of the polymer backbone.

Experimental part

The synthesis of monomers and polymers[8], and the preparation of the polymer blends of polymer **M1** with inorganic salts has been described previously[7]. As polymer **M2** is not soluble in water or methanol, equivalent amounts of polymer and salt, both dissolved in ethanol, were mixed. On mixing, precipitate was formed. The solvent was removed from the slurry. To ensure homogeneity of the blend, the residue — now readily soluble in methanol — was dissolved in methanol, and the solvent was removed once more.

Wide-angle X-ray scattering (WAXS) data were obtained on a diffractometer Kristalloflex (Siemens), using the Ni-filtered Cu-K_α line ($\lambda = 0,1541$ nm).

For small-angle X-ray scattering (SAXS) studies, the samples were placed in sealed capillaries of $0,5-1,5$ nm inner diameter. The SAXS curves were obtained via a compact Kratky camera

equipped with a one-dimensional positional detector in the range of $0,06-9°$, the width of one channel being $0,014°$.

The raw data were processed as follows: the background of the empty capillary was subtracted, taking into account the absorption. The data were smoothed by cubic polynoms with various number of points in the smoothening interval. The collimation correction on the height and on the width of the instrumental function was done by a computer program [10]. d-Spacings were calculated from the desmeared curves after subtraction of the background. The program FFSAXS [11] was adopted to calculate the correlation functions $G(R)$ by Fourier transformation of the SAXS data. To split overlapped peaks and to fit the scattering functions, the program FIT [12] was used.

Results

In the X-ray diffractograms of all samples, a number of the scattering features in the small-angle and wide-angle range is observed (Figs. $1-4$). The corresponding d-spacings for all maxima, calculated according to Bragg's law, are presented in Tab. 1.

Tab. 1. X-ray scattering characteristics of the zwitterionic polymers studied. Accuracy of d-spacings: generally $\pm 0,1-0,3$ nm, for intensive maxima $\pm 0,02-0,05$ nm. Accuracy for D values: $\pm 0,01$ nm

Polymer	Temp. in °C	d-Spacings (from small-angle peaks)			Intermolecular distance D in nm
		d_1 /nm	d_2 /nm	d_3 /nm	
A1	25	3,0	1,6	—	0,50
A1	110	2,8	1,5; 1,4	—	0,55; 0,47
M1	25	2,64	1,35	—	0,51
M1	110	2,91	1,46	—	—
A2	25	3,16; 3,06	—	—	0,52
A2	110	3,1; 3,0	—	—	0,57
M2	25	2,34	—	—	0,51
M2	110	2,34	—	—	0,52
M1 + NaI	25	3,3	1,7	1,1	0,50
M1 + NaI	110	3,3	1,7	1,1	—
M1 + KBr	25	3,2	1,67	1,1	0,50
M1 + KBr	110	3,2	1,67	1,1	—
M2 + NaI	25	2,8	1,4	—	—
M2 + NaI	110	2,8	1,4	—	—

Wide-angle X-ray scattering

In the wide-angle range, only a halo is observed for the polymers stored under ambient conditions, as illustrated in Figs. 1 and 2. The position of the top of the halo varies between $19°-21°$; its width is ca. $5°-6°$. After removal of the bound water, only minor changes of the wide-angle scattering are observed for polymers A2, M1 and M2.

Similarly after salt formation, the position of the halo is only slightly shifted to smaller angles, and the width of the halo is slightly increased. The only exception is polyacrylate A1 for which two overlapped sharper peaks are observed when the bound water is removed (Fig. 1 b, c).
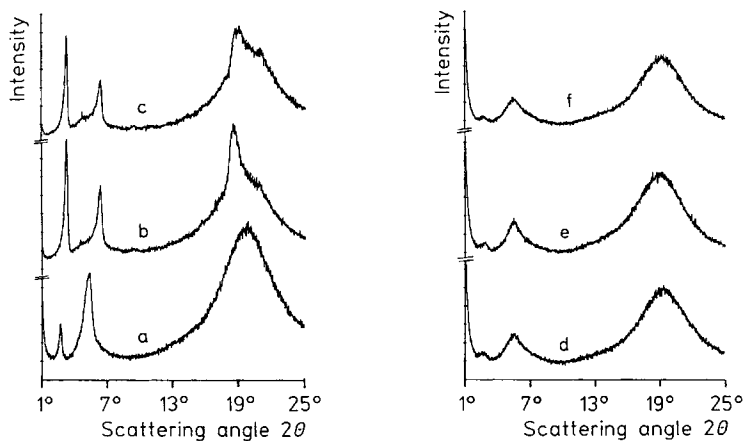
Fig. 1. Wide-angle scattering curves of polymers **A1** and **M1**: a) **A1** at 27 °C, stored at ambient conditions; b) **A1** at 147 °C; c) **A1** at 27 °C after removal of water; d) **M1** at 27 °C, stored at ambient conditions; e) **M1** at 137 °C; f) **M1** at 27 °C after removal of water
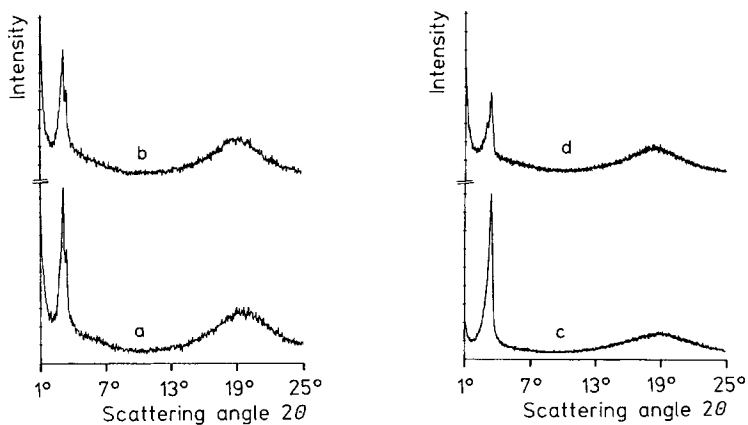

Fig. 2. Wide-angle scattering curves of polymers **A2** and **M2**: a) **A2** at 27 °C, stored at ambient conditions; b) **A2** at 157 °C; c) **M2** at 27 °C, stored at ambient conditions; d) **M2** at 157 °C

Small-angle X-ray scattering (SAXS) data of the polymers stored under ambient conditions

At small angles, the features of X-ray scattering are rich and complex, and differences between the four polymers are visible (Figs. 3 and 4). As a common feature, the SAXS curves of all systems exhibit two distinctly different scattering phenomena: a number of moderately sharp interference maxima with various intensities in the range of 1 °–8 °,

and notably increasing scattering intensities near the primary beam, the so called zero-scattering.

The positions of the interference maxima for the free zwitterionic polymers depend on the position of the ionic groups in the polymers (Figs. 3 and 4), as well as on the nature of the main chains (compare Figs. 3, or 4).

Comparing isomers with a different position of the ionic groups[8], the polyacrylate **A2** with the ionic groups close to the backbone exhibits only one broad maximum at 3,8°, whose width is 1,1°. In contrast, the isomer **A1** with the ionic groups at the end of the side chains shows two maxima: a first one with low intensity at 2,7° and a second one with higher intensity at 5,3° (Figs. 1a–4a). In analogy, the polymethacrylate **M2** exhibits only one broad maximum at 3,6°, but the isomer **M1** shows two maxima, one with low intensity at 2,8° and one with higher intensity at 5,5° (Figs. 1b–4b).
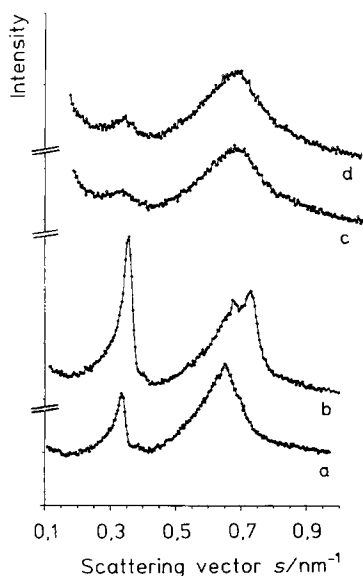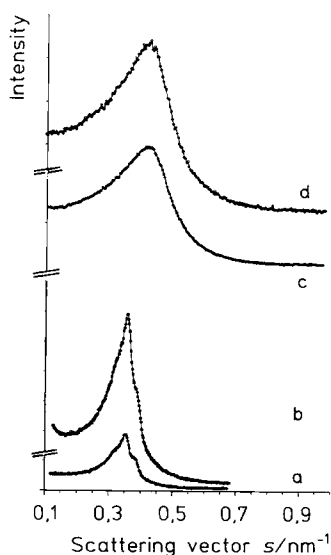

Fig. 3.

Fig. 4.

Fig. 3. Small-angle scattering curves (scattering vector $s = (4\pi/\lambda)\sin\theta$) of polymers **A1** and **M1**: a) polymer **A1** at 25 °C; b) polymer **A1** at 110 °C; c) polymer **M1** at 25 °C; d) polymer **M1** at 110 °C

Fig. 4. Small-angle scattering curves of polymers **A2** and **M2**: a) polymer **A2** at 25 °C; b) polymer **A2** at 110 °C; c) polymer **M2** at 25 °C; d) polymer **M2** at 110 °C

SAXS data of the polymers after removal of bound water

The polymers studied are brittle, hygroscopic solids. According to thermogravimetry and differential scanning calorimetry, ca. 5 wt.-% water are taken up under ambient conditions. The bound water can be removed by heating the polymers to 110 °C in vacuo or in dry nitrogene atmosphere.

After the bound water is removed, the polymers with the ionic groups attached closely to the backbone, i. e. **A2** and **M2**, exhibit the same general scattering pattern as before. Only slight shifts of the positions of the SAXS maxima to smaller angles are observed, without detectable changes in the shape of the maxima (Figs. 1 – 4, Tab. 1).

In case of the polymers bearing the ionic groups at the end of the side chain, **A1** and **M1**, the effect of the removal of water depends on the nature of the polymer backbone (Fig. 3). For the polymethacrylate **M1**, too, only minor changes of the scattering pattern are observed, with both interference maxima being slightly shifted to lower angles (Fig. 3 d). The corresponding *d*-spacings are increased by 0,3 nm. However, the SAXS pattern of the analogously built polyacrylate **A1** is changed dramatically on water removal: the first maximum is shifted to larger angles, i. e. the *d*-spacing decreases from 3,0 nm to 2,8 nm, gaining intensity. Moreover, the second broad maximum near 5° is splitted in two maxima at higher angles (Fig. 3 b).

SAXS data of the polymethacrylates blended with low-molecular-weight salts

Recently, it was shown that the polymethacrylate **M1**, in which the zwitterionic group is at the end of the side chain, is able to bind equivalent amounts of NaI and NaBr, but not of NaCl or NaF[7]. Homogeneous blends with NaI are not restricted to such polymers, but can be prepared as well from the isomers with the zwitterionic groups close to the backbone, as demonstrated by the mixtures of **M2** and NaI (Fig. 5).

The blending of the polymethacrylates is accompanied by marked changes of the SAXS patterns of the polymers (Fig. 5). Generally, the intensity of the zero-scattering is much higher when salts are bound to the polymers. When **M1** is successfully blended with salt, a complete rearrangement of the SAXS pattern is observed[7]: for blends with KBr, a strong peak at 2,7° is observed, and weaker maxima at 5,3° and 8° replacing the original two broad maxima (Fig. 5 a). A similar scattering pattern is obtained for blends of **M1** and NaI.

In contrast, the mixing of NaI and **M2** leads to less dramatic changes of the SAXS pattern. The interference maximum at 3,6° becomes less intense and is broadened. In addition, a second weak interference maximum at 7,3° is observed.

When water is removed from the polymer/salt blends, only minor changes of the scattering patterns are observed, if at all. In case of the polymer/salt blends of **M1** and KBr, the positions and the intensities of the maxima stay virtually the same when water is removed (Fig. 5 b). In case of the polymethacrylate **M2** and NaI, the main peak is strongly sharpened, but the overall appearance of the scattering pattern is unchanged (Fig. 5 f).

Discussion

The X-ray scattering data can be analysed separately in three angular regions, due to the type of information contained[10, 13]. In the wide-angle region (10°– 30°), the observed features are mainly determined by the distribution of the intermolecular distances in local packing, superposed with the corresponding intramolecular statistics. In the intermediate-angle region (1 – 8°) the scattering is determined by the formation
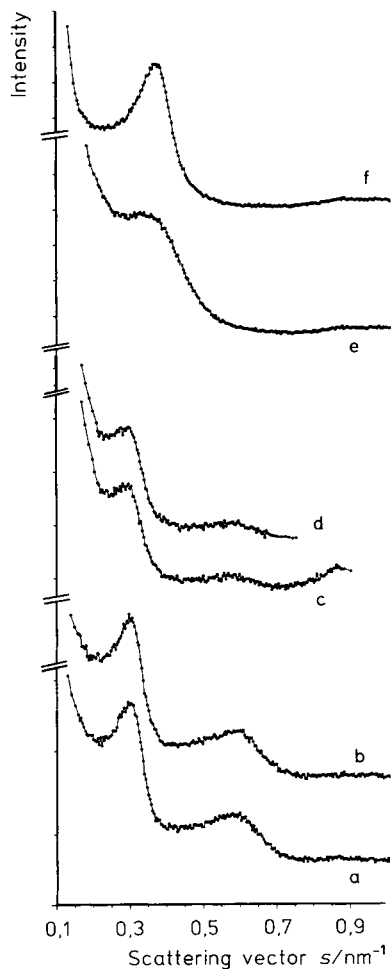
Intensity

Fig. 5.   Small-angle scattering curves of
blends of polymethacrylates **M1** and **M2**
with inorganic salts. Polymer **M1** and
KBr: a) at 25 °C; b) at 110 °C. Polymer
M1 and NaI: c) at 25 °C; d) at 110 °C.
Polymer **M2** and NaI: e) at 25 °C; f) at
110 °C

0,1   0,3   0,5   0,7   0,9

Scattering vector s/nm^{-1}

of superstructural order of $1-6$ nm in size. In the small-angle region, the zero-scattering near the primary beam is determined by the presence of long-range inhomogeneities, such as ordered domains in disordered matrices or coiled macromolecules in solution[10]. As the changes of scattering in these angular regions are very different for the polymers studied, they are discussed separately.

Wide-angle scattering

As known from amorphous, flexible polymers, the presence of a diffuse halo in the wide-angle region is caused by short-range order in the intermolecular lateral packing of the macromolecular fragments[14]. The position of the maximum corresponds to the most probable intermolecular distance D of local contacts. Assuming densely, quasi-hexagonally packed cylinders, D can be approximated by the modified Bragg

equation[14, 15] $D = 1,117/(2 \sin\theta)$. Values of D in the range of $0,47-0,57$ nm are calculated for the polymers studied (Tab. 1), which are characteristic of amorphous polymers with methylene-containing fragments[15]. The width of the diffuse halo is determined by the distribution of the intermolecular contacts of the different fragments and by the level of the distortion of translational order in the local packing[14, 15]. The observed widths of $4°-6°$ correspond to liquid-like short-range order with correlations expanded upto $3-4$ coordinate spheres. The values of the correlation length ζ are in the range of $0,3-1$ nm (see Tab. 2). Thus considering the local packing, the studied ionic polymers are typical amorphous systems with short-range order.

On heating and removal of bound water, or on salt formation, the parameters of the short-range order are virtually unchanged for most of the studied polymers (Tab. 2). Only in case of the polyacrylate **A1**, the removal of the bound water leads to rearrangement of the intermolecular packing: two distinct sets of the intermolecular distances are observed with $D = 0,55$ nm and $D = 0,47$ nm, as derived from the splitting of the WAXS maximum on the two overlapped peaks (Fig. 1 b, c). There are several explanations for this behaviour, e. g., two different types of intermolecular lateral packing of different fragments can be considered, or a change of symmetry of the local packing, e. g. from quasi-hexagonal to orthorhombic.

Tab. 2. Calculated correlation lengths of the zwitterionic polymers: ξ_D = correlation length of WAXS maximum; ξ_1, ξ_2 = correlation lengths from zero-scattering

Polymer	Temp. in °C	Correlation lengths		
		ξ_D/nm	ξ_1/nm	ξ_2/nm
A1	25	0,5	2,0	0,4
A1	110	0,9	—	—
M1	25	0,4	2,0	0,7
M1	110	0,4	—	—
A2	25	0,4	—	—
A2	110	0,3	—	—
M2	25	0,5	3,5	1,4
M2	110	0,4	—	—
M1 + NaI	25	—	1,5	0,3
M1 + KBr	25	—	1,5	0,3
M2 + NaI	25	—	1,5	0,3

Zero-scattering

For ionic polymers, the existence of the zero-scattering is often simply ignored, and all conclusions are confined to the analysis of interference peaks. Basically two major approaches are used for the analysis of the zero-scattering for ionic systems[16-19]: The first one is the analysis of the scattering in "diluted" approximation, with the determination of the Guinier radius of the inhomogeneities. This approach can be used for ionic systems with low concentration of the ionic groups, but it is not valid for bulk

systems with close packing of ionic microregions. Thus, it cannot be applied to the zwitterionic polymers under investigation.

The second approach is the Debye-Zernike one for systems with randomly distributed inhomogeneities. This type of analysis was applied for the obtained scattering data. It is described in real space by spatial correlation functions of the form [20]

$$G(R) \sim \exp(-R/\xi) \tag{1}$$

The corresponding scattering function in reciprocal space is given by

$$I(s) \sim (1 + \xi^2 \cdot (s - s_0)^2)^{-2} \tag{2}$$

where ξ is the corresponding correlation length, $s = (4\pi/\lambda)\sin\theta$ is the scattering vector, and s_0 is the position of the scattering peak. For the analysis of zero-scattering, $s_0 = 0$. The value of ξ is a measure of the translational order in the system. For systems with spatial correlations described by Eq. (1), the size L of the ordered regions can be estimated [21] by $L \approx 3\xi$.

The angular dependences in the coordinates $I^{-0.5}$ vs. s^2 are illustrated for polymers **M1** and **A1** in Fig. 6. The spherically symmetric correlation functions $G(R)$ which were calculated from zero-scattering are plotted in a half logarithmic scale in Fig. 7.
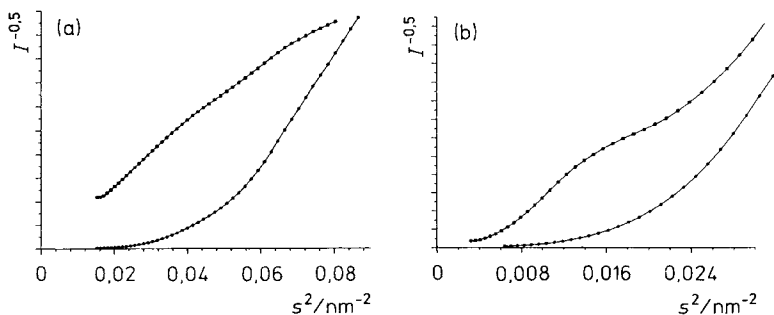

Fig. 6. Zernike analysis for zero-scattering: a) lower curve = polymer **A1**, upper curve = polymer **M1**; b) polymer **M1** blended with salt: upper curve = KBr blend, lower curve = NaI blend

As evident from Figs. 6 and 7, the spatial correlations and the corresponding scattering behaviour are complex and cannot be fitted by simple Eqs. (1) or (2) with one parameter only; but the data may be described with two different parameters of ξ, ξ_1 and ξ_2 (see Tab. 2). Such a behaviour can be due to the presence of inhomogeneities of two different sizes [10, 14, 15]. The characteristic correlation lengths of the different sizes ξ_1 and ξ_2 are in the range of $2-4$ nm and $0.4-1.4$ nm for the pure polymers, and of 1,5 nm and 0,3 nm for the polymer-salt mixtures (see Tab. 2). Noteworthy, the values are higher for pure polymer **M2** than for pure polymer **M1**, but they become equal after salt formation (Tab. 2). The inhomogeneities of the larger size
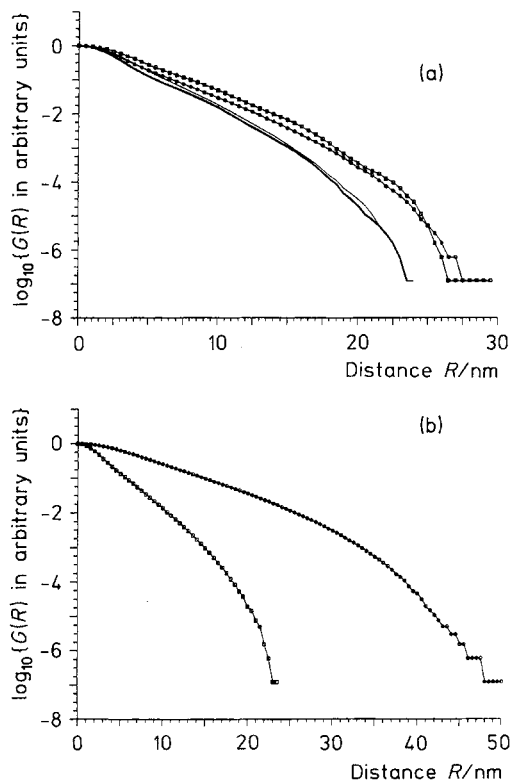
Fig. 7. Debye analysis of $G(R)$. a) From top to bottom: polymer **A1**, polymer **M1**, blend of **M1** and KBr, blend of **M1** and NaI; b) top: polymer **M2**, bottom: blend of **M2** and NaI

can be attributed to the formation of a lamellar superstructure, as discussed below. The presence of large-size inhomogeneities has been detected and discussed recently for other systems[18]. The small-size inhomogeneities can be connected with the spatial correlations of the ionic groups. This type of inhomogeneity is frequently observed for ionic polymers, and it is attributed to small regions of aggregated ions[22].

The analysis of the calculated correlation functions enables the evaluation of the shape of the inhomogeneities. For a spherical form, the characteristic function $P(R)$ = $G(R) \cdot R^2$ should be symmetric. $P(R)$ should have a maximum at $R = R^0$ and be zero at $R = 2R^0$, with R^0 being the radius of the inhomogeneities[10]. For inhomogeneities with asymmetric shape, $P(R)$ and $P(R)/R$ are asymmetric functions with characteristic features for various shapes[13]. With this approach we have calculated the characteristic functions $P(R)/R$ (Fig. 8). The asymmetric shape of all calculated functions are characteristic of plate-like particles. Taking the maximum of the curve for the thickness and the x-axis intercept for the lateral size[13], thicknesses of the platelets in the range of $7-15$ nm and lateral sizes in the range of $25-50$ nm are estimated by curve analysis (Fig. 8). I.e., the lateral sizes of the inhomogeneities are $3-4$ times larger the longitudinal ones.

A strict evaluation of the shape of the scattering regions would require the analysis of scattering data of oriented samples. But up to now, well oriented samples of the

zwitterionic polymers could not be prepared. Below we will consider additional arguments for the lamellar shape of the ordered regions in the polymers studied.
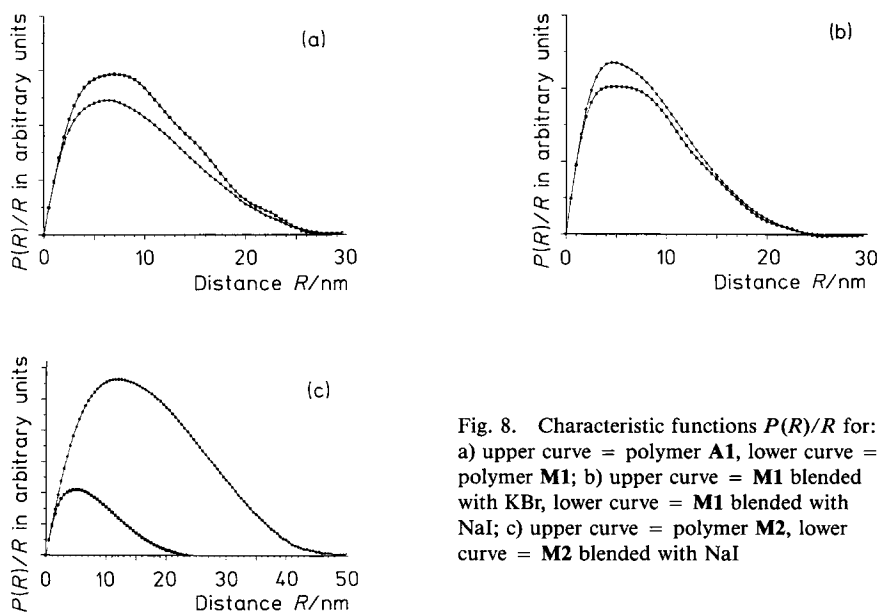

Fig. 8. Characteristic functions $P(R)/R$ for: a) upper curve = polymer **A1**, lower curve = polymer **M1**; b) upper curve = **M1** blended with KBr, lower curve = **M1** blended with NaI; c) upper curve = polymer **M2**, lower curve = **M2** blended with NaI

Interference maxima

In the intermediate scattering region, the general analysis of the scattering patterns reveals a wide spectrum of superstructures for the various polymers. The structural parameters depend on the chemical structures of the polymers, on the presence or absence of water, and on the presence or absence of added salts. Thus, all polymers exhibit their individual d-spacings (Tab. 1). The individual character is reflected by the changes induced by added salts or removal of bound water, too. Whereas the addition of salt to **M1** results in a complete change of the scattering pattern, polymer/salt blends of **M2** give similar patterns as the pure polymer.

Analysing the positions of SAXS maxima for the various pure polymer systems, the complex distribution of the intensity of the interference maxima cannot be described by a simple model of packing of the macromolecular fragments (for example single- or double-layered). Furthermore, the values of d cannot be correlated easily with the lengths of the macromolecular fragments (e. g. 2,6 nm for the fully extended length of the side groups). This is only possible by the full analysis of the SAXS data with calculations of the density distributions and the construction of the corresponding computer molecular models as discussed later[9].

The situation is simpler for the polymer/salt blends. They all match the formal relationship for positions of various order of reflection from lamellar structures

(Tab. 1). Indeed, for the blends of **M1** and KBr, **M1** and NaI, and **M2** and NaI, the ratios $d_1:d_2:d_3$ are close to $1:1/2:1/3:1$, respectively. These findings are in agreement with the discussion above, supporting the formation of lamellar structures of the zwitterion polymers.

The removal of the water influences the superstructures individually. Comparing the four polymers studied, it has only major effects on the superstructure of polyacrylate **A1**, bearing the ionic group at the end of the side chains, the scattering pattern of which is completely changed. This indicates a basic structural rearrangement in this polymer during the removal of water molecules. As in **A1** the bulky ionic groups are distant from the backbone and the polyacrylate backbone is much more flexible than the polymethacrylate one, it is understandable that the structural rearrangement is observed for **A1** rather than the other three polymers. Interestingly, the new type of scattering pattern obtained is very similar to the one observed for polymer **M1** after mixed-salt formation. These results emphasize that several factors contribute to the superstructure formed: not only the molecular architecture, i.e. the distance of the ionic groups from the backbone, but as well the nature of the backbone and the presence or absence of polar additives such as water or salts. The results illustrate instructively that subtle changes of these factors may result in major differences in superstructures, even for closely related systems. The perfection of the superstructural order and the corresponding structural rearrangements will be discussed in detail elsewhere, in the context of the proposed models of molecular packing[9].

Conclusions

The zwitterionic polymethacrylates investigated, with different positions of the ion-containing groups, are typical amorphous-like systems with liquid-like order in the local lateral packing of the chains. The same is true for the blends of the polymers and inorganic salts. The corresponding short-range order is expanded only for $3-4$ neighbouring structural elements. However, structures with higher local order are formed when the polymethacrylate backbone is replaced by the polyacrylate one.

In all the polymers, two types of inhomogeneities exist which are of large and small size. The large-size inhomogeneities are attributed to spatial correlations in the ordered structures of the macromolecular fragments. The small-size inhomogeneities are due to the formation of some spatial order of the ionic groups. The formation of the well-defined lamellar structures for the polymer/salt blends and the asymmetric shape of the characteristic functions point to a plate-like shape of the ordered regions in the ionic polymers studied.

From the analysis of the samples some general conclusions about the relationships between the chemical structure of the macromolecular fragments and the corresponding features of structural state and rearrangements are derived. For poorly ordered systems with the ionic groups attached near the backbone, the addition of inorganic salts or the removal of water causes only minor rearrangements of the structural order. Shifting the position of the ionic groups from the end of the side chain close to the polymer backbone, a complete rearrangement of the molecular packing of the fragments can be observed on addition of inorganic salts or on the removal of water.

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