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The structural order of some novel ionic polymers, 2[a)]

Models of molecular packing

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SUMMARY:

The molecular packing and spatial correlations of two isomeric zwitterionic polymethacrylates and one polyacrylate analog are studied by means of X-ray analysis and conformational calculations. The analysis of the correlation functions and density distribution profiles suggest a double-layered molecular packing which is discussed for the three polymers investigated, with respect to their different chemical structures. Whereas the zwitterionic polymethacrylates studied exhibit liquid-like short-range order, the polyacrylate analog exhibits an ordered double-layered superstructure.

Introduction

Recently, a set of isomeric zwitterionic polyacrylates and polymethacrylates was studied by small-angle X-ray scattering, to elucidate the role of the chemical variations onto the structural order of the polymers[1)]. Now, the X-ray analysis is extended by calculation of the correlation functions and of the corresponding density distribution profiles. Comparing the calculated data with the experimental ones, models of the local packing of the molecular fragments are proposed, and the corresponding parameters of the structural order are discussed. The zwitterionic polymers studied are shown in Scheme 1.

Experimental part

The synthesis and characterization of the studied polymers and the experimental X-ray data were reported previously[1–3)].

The program FFSAXS was adopted to calculate the correlation functions by Fourier transformation of the previously processed small-angle X-ray scattering data[1,4)]. In order to calculate the normalized one-dimensional correlation functions $G(x)$, the cosine Fourier transform of the Lorentz-corrected scattering data $I(s)$ was used in the form:

$$G(x) = \int s^2 \cdot I(s) \cdot \cos(sx)\,\mathrm{d}s \Big/ \int s^2 \cdot I(s)\,\mathrm{d}s \qquad (1)$$

where $s = (4\pi/\lambda)\sin\theta$ is the scattering vector.

[a)] Part 1: cf. ref.[1)]

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For the calculation of $G(x)$, X-ray data in the range of 0,06° to 9° were used. The simulated correlation function $G^*(x)$ is a self-convolution of the density distribution along the normal to the layered planes[5,6] $\rho(x)$, expressed by

$$G^*(x) = \int \rho(x') \cdot \rho(x' - x) \mathrm{d}x' \tag{2}$$

Thus by direct calculation of the integral using Eq. (2), it is possible to model the function $\rho(x)$ comparing the simulated correlation functions $G^*(x)$ with $G(x)$ derived from experimental data by Eq. (1). A detailed description of the procedure is given in refs.[7,8] The values of the residual factor R for the model profiles are 3% – 10%.

To calculate the correlation lengths in order to characterize the supermolecular ordering we have analyzed the damping of $G(x)$ by means of the Debye approach[5,6]. $G(x)$ is approximated in the form

$$G(x) = \exp(-x/\xi) \cdot \cos(2\pi x/d) \tag{3}$$

where d is the main period of oscillation of $G(x)$.

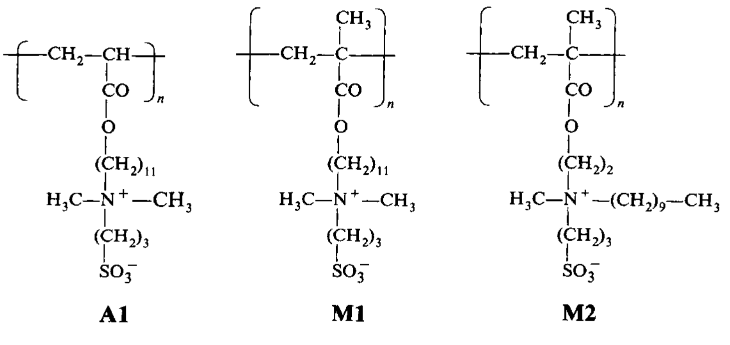
To model a possible packing of molecular fragments, and to calculate the intra- and intermolecular distances, computer models are built by means of the program Insight II[9]. The most favourable conformations of the monomeric units of the macromolecules are calculated by the conformational program Discover and by the quantum-mechanical program MOPAC 5.0 on a Silicon Graphics computer system[9].

Results

The calculated functions $G(x)$ are shown in Figs. 1 – 4. All of them have the shape of damped oscillating functions. Damping to zero is achieved at distances of L = 10 – 30 nm (Tab. 1).

A pure cosine-like damping shape of $G(x)$ is observed for the polymethacrylate **M2**, for the pure polymer as well as for equivalent mixtures of the polymer and NaI. For the pure polymer only 5 damping maxima are observed up to a distance L = 12 nm. The shape of $G(x)$ is not changed after water is removed by heating the sample to 110 °C. The peaks of $G(x)$ are broader and slightly shifted when **M2** is mixed with NaI (Fig. 1).

Scheme 1:



A1 **M1** **M2**

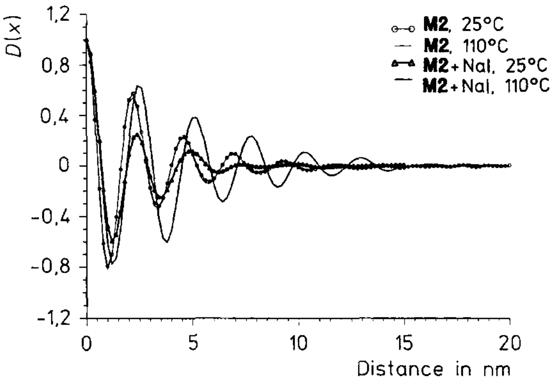


Fig. 1. One-dimensional correlation functions $D(x)$ for **M2**: pure polymer at 25 °C; pure polymer at 110 °C; blend with NaI at 25 °C; blend with NaI at 110 °C

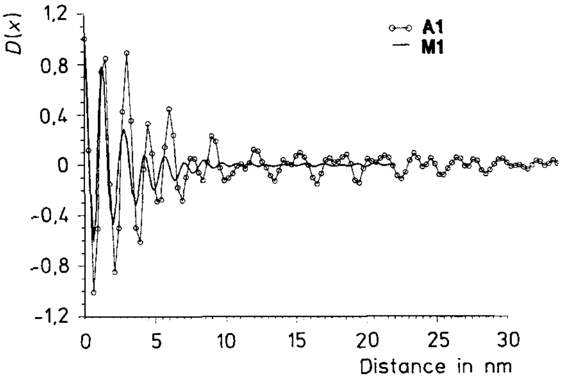


Fig. 2. One-dimensional correlation functions for **M1** and **A1** at room temperature

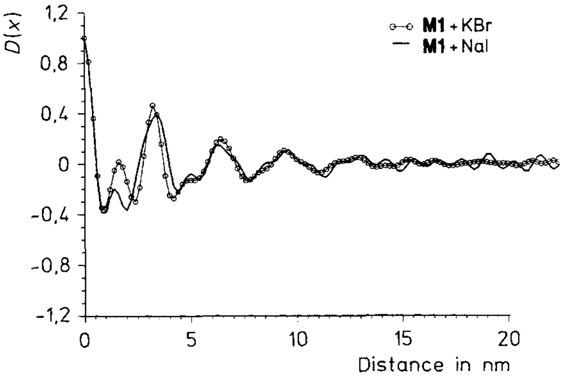


Fig. 3. One-dimensional correlation functions for **M1** mixed with KBr and NaI, respectively, at room temperature

For the polymethacrylate **M1**, the shape and the character of damping of $G(x)$ is similar to polymer **M2**, as described above.

For the polyacrylate **A1**, the shape of $G(x)$ differs markedly from both polymethacrylates (Figs. 2 and 4): a double peak is observed with lower intensity of the first peak

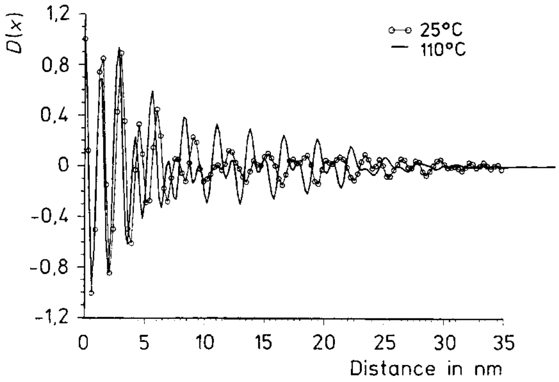


Fig. 4. One-dimensional correlation functions for **A1** at 25 °C and 110 °C

Tab. 1. Structural characteristics of the studied polymers; l_1 = regions of backbone packing, l_2 = regions of packing of ionic groups, l_3 = regions of alkyl chain packing (see Fig. 6). Accuracy of d and l values ±0,1 nm, of L values ±2 nm, of correlation lengths ±0,5 nm

Polymer	Temp. in °C	*d*-Spacing		Zero damping distance	Corre-lation length	Sizes of packing subregions			Dipole moment in Db
		d_1/nm	d_2/nm	L/nm	ξ_1/nm	l_1/nm	l_2/nm	l_3/nm	
A1	25	3,0	1,4	30	9	0,6	0,8	1	28
A1	110	2,8	1,3	30	13				
M1	25	1,3	—	10	3	0,4	0,4	0,9	28
M1	110	1,3	—	10	3				
M2	25	2,2	—	12	4	0,8	—	1,4	27,8
M2	110	2,2	—	12	4	0,8	—	1,4	
M1 + NaI	25	3,4	1,5	15	4,5	0,8	0,8	1,2	
M1 + NaI	110	3,2	1,4	15	4,5				
M1 + KBr	25	3,2	1,6	15	5	0,8	0,9	1,1	28
M1 + KBr	110	3,2	1,6	15	5				
M2 + NaI	25	2,4	—	10	3	1,2	—	1,2	
M2 + NaI	110	2,5	—	16	6				

in one period. Furthermore, the oscillations are expanded to much greater distances (up to 30 nm) (Tab. 1). A similar picture is observed after removal of the water, but the maxima are sharper and are slightly shifted to shorter distances. One additional density wave is observed, too.

In contrast to **M2**, as a result of the salt formation of **M1** with KBr and NaI, the shape of the correlation functions differs significantly from the ones calculated for the free polymer (Fig. 3). $G(x)$ exhibits a double peak in the period with low height of the first of them. This is similar to the behaviour of $G(x)$ for the polyacrylate **A1**. Such a distribution is preserved up to distances of 14–16 nm (Tab. 1). Removal of water does not change the shape of the correlation functions.

The values of ξ calculated from the analysis of the damping of the correlation functions according to Eq. (3) vary from 3–4 nm for **M1** and **M2**, respectively, to

9–13 nm for **A1** (Tab. 1). The lowest value of ξ = 3 nm is observed for **M1**, the highest value of 13 nm is found for the polyacrylate **A1** after the removal of water.

Conformations and the spatial properties of the fragments

Conformational analysis was done for two linked monomeric units, i. e. dimers. For polymers **A1** and **M1** with terminal betaine groups at the end of the side chains, the alkyl side chains are virtually fully extended with *trans*-conformation of the C—C bonds, and are arranged almost orthogonally to the backbone (Fig. 5).

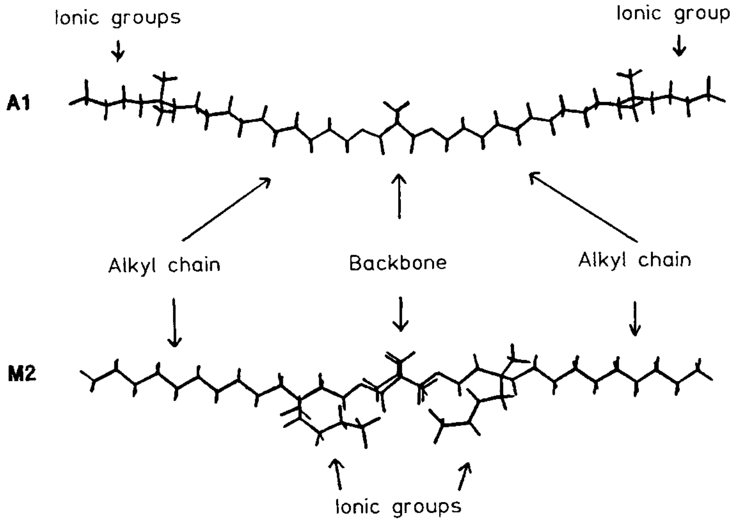


Fig. 5. Computer models of the arrangement of macromolecular fragments of **A1** and **M2**

The overall conformation of the monomeric units in **M2** with the position of the betaine groups near the backbone is similar to **M1**. However the orientation of the sulfonate groups differs significantly. Further, an orthogonal arrangement of the side chain is preserved only if 2–3 *gauche* conformers are incorporated next to the ammonium group.

Concerning the dipole moments, the calculated absolute values for the monomeric unit are virtually identical for all systems, viz. about 28 Db (Tab. 1). However the corresponding vectors for the dipole moments have different orientations. In the case of **A1** and **M1**, with the betaine groups at the end of the side chains, the dipole moment is oriented along the alkyl chains, i. e. orthogonal to the backbone. In the case of **M2** with the betaine group near the backbone, the dipole moment is oriented approximately parallel to the backbone.

Discussion

Density distribution and models of molecular packing

From a general point of view, the small-angle X-ray scattering patterns studied can be divided in two groups. In the first group which includes the polymers **M1** and **M2**, only one broad peak is observed, whereas in the second group two very intensive peaks are found, of which the second one is slightly shifted to the exact Bragg position $d/2$ (see Tab. 1 and ref.[1]). Also, in the first group a pure cosine-like shape of the correlation functions $D(x)$ is observed, while the second group exhibits complex shapes of $D(x)$. According to the classic treatment of X-ray scattering[5, 10, 11] we can expect a pure cosine-like shape of the density distributions for the first group. The same conclusion can be drawn from the analysis of the one-dimensional correlation functions[12]: A simple "two-phase" density distribution profile should lead to a pure damped cosine-like shape of the corresponding correlation functions. In the second group, intense second-order reflections are present, and the shift of their position points to a strong modulation of the structural factor, and thus to a complex density distribution in the systems studied. The same conclusion can be derived from the deviation of the shape of the one-dimensional correlation functions from the pure damped cosine-like ones[5, 7, 10–12]. Only a direct simulation of $D(x)$ by a self-convolution of trial profiles with additional density waves will provide information on $\rho(x)$. Based on these considerations, the parameters of the density distributions of the investigated systems were calculated, which are discussed below.

The analysis of the data is most straightforward for the polymethacrylate **M2**. The simple sine-like shape of $G(x)$ can be explained by a simple "two-phase" model[5] of the density distribution with higher density of packing of the betaine groups and of the backbones, and with lower density of packing of the alkyl chains (Fig. 6). The corresponding lengths of the regions with high density (l_1) and with low density (l_3) are equal to 1,4 nm and 0,8 nm, respectively (Tab. 1). The packing of the molecular fragments in double layers with partial overlapping of the alkyl side chains matches well with the simulated density profile, $\rho(x)$, as illustrated in Fig. 6a.

When water is removed, the parameters of density distribution l_1 and l_3 are preserved (Tab. 1). Accordingly, the distribution of the water molecules in the molecular packing of the fragments must be irregular.

In the methacrylate analog **M1**, a shape of $\rho(x)$ is observed similar to the "two-phase" system (Fig. 6a). However if analyzed more precisely, a simple double-layer structure — as found for **M2** — does not match $\rho(x)$ satisfactorily; but the calculated $\rho(x)$ is well fitted if a model of molecular packing with a systematic shift of neighbouring molecular fragments is assumed (Fig. 6b). The main periodicity of 5,2 nm in this model is determined by the distances between two backbones in one plane for conventional double-layered packing. Due to the presence of neighbouring molecular fragments shifted by roughly half a period, we observe in addition a pseudo-periodicity of 1,3 nm (Fig. 6b). It should lead to an increase in the intensity of the corresponding reflection with $d = 1{,}3\,\text{nm}$ as compared to $d = 5{,}2\,\text{nm}$ and 2,6 nm. Such a distribution of the scattering intensity is indeed observed experimentally[1]. As found for the isomeric polymer **M2**, the parameters of density distribution, l_1 and l_3, are preserved for

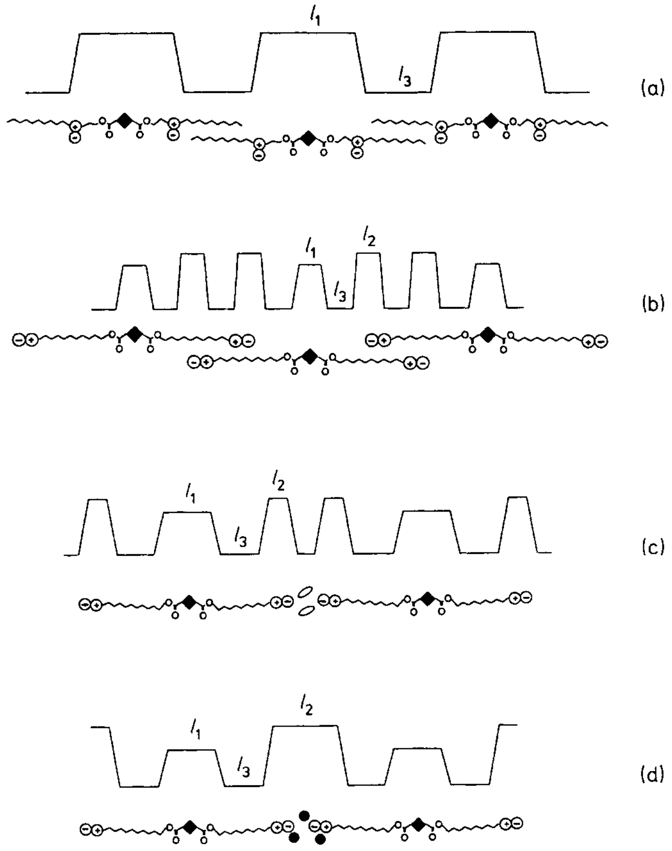


Fig. 6. Density distribution along the normal to the layered planes $\rho(x)$ and corresponding models of molecular packing; a) **M2**, b) **M1**, c) **A1**, d) **M1** mixed with salt. Symbols used: ◆ = polymer backbone; ⊖ = anionic sites; ⊕ = cationic sites; /\/\/\ = alkyl chain; ○ = water molecules; ● = inorganic ions

polymer **M1** when water is removed. Accordingly, the distribution of the water molecules in the molecular packing of the fragments must be irregular.

The correlation functions of **A1** exhibit a complex shape which cannot be explained by a simple "two-phase" model[8]. The result of the best fit of $\rho(x)$ is shown in Fig. 6c, yielding a model with four regions of different density.

In this profile, higher densities are observed in two regions: in the regions of the polymer backbones and in the regions of the betaine groups. The alkyl chains form a region of lower density, as do the water molecules which are localized between the terminal ionic groups of the side chains, giving rise to an additional region with lower density between neighbouring layers (Fig. 6c). Such a density distribution is determined by the formation of highly segregated regions with separated packing of the different macromolecular fragments: polymer backbones, alkyl side chains, betaine groups and bound water. Very similar microphase-separated lamellar structures have been observed for some smectic liquid-crystalline polyacrylates and polymethacrylates with long spacers[8)].

The length of the region with lower density, l_3, is determined for the polyacrylate **A1** by the length of the alkyl side chains, between the backbone and the terminal betain group. The conformation of the sulfobetain groups[13)] could not be determined exactly from $\rho(x)$: both the extended and the folded conformation of the betain group fit to the observed geometric parameters. The main periodicity d = 6 nm of the proposed density distribution corresponds to a double-layered packing.

When water is removed from **A1**, the d-spacing decreases by 0,4 nm (Tab. 1). As the region formed by the bound water molecules is missing now, a model with only three regions of different density is obtained, and the now contacting betain groups exhibit a slightly higher packing density. Although this model satisfies the main features of $G(x)$, the additional density wave at higher distances and the split of one of the maxima in the SAXS curve (see Part 1)[1)] have not been taken into account. Hence in reality, the structural order of the system must be somewhat more complex than the one discussed above, or an additional, different structure is present.

Polymers mixed with inorganic salts

Several polymeric sulfobetaines have been shown to form homogeneous blends with some inorganic salts[1,2,14)]. Analysing the data of mixtures of the polymethacrylate **M2** with NaI, some changes of the density distribution profile compared to the pure polymer are observed: according to these changes, the length l_1 and the density of packing of the betaine groups are increased (Tab. 1). This points to the incorporation of the added salts in the vicinity of the betaine groups, and close to the polymethacrylate backbone, as discussed for bound water above.

In the case of polymethacrylate **M1**, the shape of the one-dimensional correlation functions for polymers mixed with NaI and KBr looks very similar to the one of the pure polymer, too: a main peak is observed at 3,2 – 3,4 nm, and a minor one at 1,5 – 1,6 nm (Fig. 3). Such a shape of $G(x)$ is attributed to a complex density distribution profile of the type which was discussed above for the pure polymer, i. e. with separated, packed backbones and terminal ionic groups (Fig. 6d).

The profiles of $\rho(x)$ fit to the double-layered packing of the molecular fragments with dense packing of the terminal groups (Fig. 6d, Tab. 1). The parameters of molecular packing are very similar for polymers mixed with KBr and NaI (Tab. 1).

Spatial correlations

As could be deduced from the correlation lengths and the sizes of the ordered regions, L, for all polymethacrylates in pure form and mixed with salts, the ordering in the arrangement of the molecular fragments is expanded only up to 10 – 16 nm (Tab. 1). It means that the ordered regions include only 2 – 3 neighbouring fragments. This is typical of amorphous polymers with short-range ordering[8)].

The spatial correlations in the arrangement of heterogeneities is expanded over the "short-range" limit only for the acrylate polymer **A1**: the value of L is greater than 30nm. Thus 5–6 neighbouring molecular fragments are arranged in double-layered packing with the order preserved. Such a level of perfection exceeds that in common liquid-like systems. It is very similar to the observed one in distorted, layered structures of liquid-crystalline side-chain polymers[8]. Hence, the packing of the side fragments in the ionic polyacrylate can be described as smectic-like layered structure.

Conclusions

Only the short-range order in local and supermolecular packing of side fragments is realized in the studied ionic polymethacrylates. From this point of view these systems are typical amorphous polymers. The observed various scattering effects are due to the formation of double-layered packing of molecular fragments of various type, with extension of the spatial correlations only to 2–3 neighbouring fragments.

Contrarily, in the ionic polyacrylate bearing in the side chain terminal betaine groups, more ordered smectic-like structures are formed with correlations in the arrangement of the fragments expanding up to 30nm. The observed structural differences are typical of similar polymers with ordered structures[8].

A number of structural rearrangements is observed as a result of the changes in the chemical structures of the molecular chains which can be summarized as follows:

i) Shifting the position of the betaine group from the terminal position in **M1** to a position near the polymer backbone in **M2** leads to a rearrangement of the supermolecular ordering. In the latter case a double-layered packing with considerably overlapped alkyl side chains is obtained, while in the former case a double-layered packing of the molecular fragments with a shift of the neighbouring macromolecules of half of the period is observed. Despite the structural differences, in both methacrylate systems bound water molecules are irregularly distributed in the superstructures.

ii) The change of the methacrylate backbone of **M1** to the more flexible acrylate backbone of **A1**, without changes in the chemical structure of the side chains, leads to a full rearrangement of the packing of the side chains, and the formation of more perfect superstructures. The localization of the ionic groups at the end of the alkyl side chains enables the formation of highly segregated structures. This results from microphase separation of the polymer backbones and of the fragments of the side chains. The complex density distribution modulation in such a system is due to the formation of regions with separated, packed polymer backbones, terminal ionic groups and water molecules, forming the interlayers between the terminal ionic groups of neighbouring fragments.

iii) For polyacrylate **A1** with the highest level of perfection of layered order, the presence or the absence of water molecules plays an essential role in the formation of the double-layered structures. In this system, the water molecules are included in the layered packing and influence the corresponding X-ray optical properties.

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1) P. Köberle, A. Laschewsky, V. V. Tsukruk, *Makromol. Chem.* **193**, 1815 (1992)

2) P. Köberle, A. Laschewsky, T. D. Lomax, *Makromol. Chem., Rapid Commun.* **12**, 427 (1991)

3) A. Laschewsky, I. Zerbe, *Polymer* **32**, 2070 (1991)

4) C. G. Vonk, *J. Appl. Cryst.* **8**, 340 (1975)

5) *"Small-angle X-ray scattering"*, O. Kratky, O. Glatter, Eds., Academic Press, New York 1982

6) D. I. Svergun, L. A. Feigin, *"Small-angle X-ray and neutron scattering"*, Academic press, New York 1986

7) V. V. Tsukruk, Yu. S. Lipatov, V. V. Shilov, *Macromolecules* **19**, 1308 (1986)

8) V. V. Tsukruk, V. V. Shilov, *"Structure of Polymeric Liquid Crystals"*, Naukova dumka, Kiev 1990

9) *Insight II*, Biosym. Techn., San Diego, CA 1991

10) R. Hosemann, S. N. Bagchi, *"Direct analysis of Diffraction by Matter"*, North Holland P. C., Amsterdam 1962

11) A. J. Leadbetter, in *"Thermotropic Liquid Crystals"*, G. W. Gray, Ed., Wiley & Sons, New York 1987

12) G. R. Strobl, M. Schneider, *J. Polym. Sci., Polym. Phys. Ed.* **18**, 1343 (1980)

13) E. Marchal, *Polymer* **32**, 297 (1991)

14) A. Mathis, Y. L. Zheng, J. C. Galin, *Makromol. Chem., Rapid Commun.* **7**, 333 (1986)