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Polymer 42 (2001) 3523–3532

polymer

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Liquid crystalline polyanion/polycation/water systems

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Received 27 April 2000; received in revised form 12 September 2000; accepted 29 September 2000

Abstract

The phase diagrams of polyanion/polycation/water systems with varying acidity of the ionic groups of the polyanion were investigated. The phase diagram of the ternary system poly(styrenesulfonic acid) (NaPSS), poly(diallyldimethylammonium chloride) (PDADMAC) and water is dominated by a macroscopic phase separation due to the formation of polyelectrolyte complexes. A transition to macroscopic homogeneous systems is only observed for concentrated samples, if one component is in excess. By replacing NaPSS by a statistical copolymer with maleic acid, the region of macroscopic phase separation becomes smaller and macroscopically homogeneous one phase systems are now formed over a much wider range of the phase diagram.

Concentrated, macroscopically homogeneous polyanion/polycation/water systems were investigated by comparing them to the corresponding concentrated aqueous polyelectrolyte solutions by means of polarized-light microscopy, differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS) and electron microscopy (EM). Concentrated aqueous polyanion solutions show a temperature induced spherulitic crystallization. The addition of a cationic polyelectrolyte decreases the crystalline order and induces the formation of a temperature controlled liquid crystalline phase.

Keywords: Polyelectrolyte complexes; Phase diagram; Liquid crystals

1. Introduction

Polyelectrolyte complexes are formed when diluted aqueous solutions of oppositely charged polyelectrolytes are mixed [1]. The process of the complex formation is entropy-driven due to the release of the counterions, which were “bound” to the ionic groups before. Depending on the reaction conditions, the complex particles can vary from highly swollen colloidal hydrogels to compact precipitates [2]. The phenomena of phase separation can be suppressed by crossing critical overall polymer concentration, which is system specific (borderline concentration). Along this borderline, the ionic strength, which arises from the free counter-ions, is approximately constant. In the case of weak Coulombic interactions, for example in the Na-polyacrylate/poly(ethylene imine)/water system, the borderline polymer concentration is in the order of 0.15 wt% [3].

Using the polyelectrolyte components Na-polyacrylate and poly(diallyldimethylammonium chloride) (PDADMAC, i.e. a highly charged polycation with quaternary N-functions) the borderline polymer concentration is shifted to 14 wt% corresponding to a borderline ionic strength of $\cong 2$ mol/l [4]. This observation shows that the acidity of the functional groups as well as the charge density along the backbone chain is of great importance for the phenomena of phase separation.

It’s well known that polymers with rigid or semi-rigid main chains can form liquid crystalline states. The unique parameter of the chain extended polymers is the persistence length q. For example cellulose and its derivatives are semi-rigid chain polymers with q-values in the order of 25 nm [5] and can form lyotropic liquid crystals in appropriate solvents. Semi-rigid polyelectrolytes, which are highly extended compared to randomly coiled polymers, may also impart liquid crystallinity to their solutions. For example linear viruses (a unique group of nucleic acids) are an interesting and rather spectacular class of lyotropic liquid crystal polyelectrolytes. Like all such viruses, the tobacco mosaic virus has a helical structure and q-values of 300 nm were determined by using dynamic light scattering [6].

The possibility of polyelectrolytes to form ordered structures in dilute systems has been reported by several authors [7,8]. Less attention has been paid to the molecular arrangements of polyelectrolytes in highly concentrated aqueous solutions. However, xanthans reveal a viscosity maximum

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PII: S0032-3861(00)00705-9

Table 1
Properties of the used polyelectrolytes

Polyelectrolyte	M_n(g/mol)	M_w(g/mol)	M_w/M_n
Anionic			
NaPSS	16 900	82 200	3.88
NaPSS-MA	9900	25 000	1.53
Cationic			
PDADMAC	72 200	151 000	1.09

in the concentration range of 3–8 wt% resulting from the formation of a semicrystalline helical structure. Hatakeyama et al. [9–11] studied the molecular behavior of semirigid polyelectrolytes, i.e. cellulose sulfate, carboxymethylcellulose, lignosulfonate, and xanthan in highly concentrated aqueous solutions by means of differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (NMR) and polarized-light microscopy. The authors attributed the two endothermic peaks of the DSC heating curves to the melting of the free water and to the transition to the isotropic liquid state, respectively. Supported by characteristic textures, observed by polarized-light microscopy, the authors assume a temperature dependent formation of a liquid crystalline phase. However, this interpretation was not confirmed by small-angle X-ray diffraction (SAXS) measurements.

Inspired by this example, the aim of this work was to investigate phenomena of structure formation in concentrated polyanion/polycation/water systems. First the behavior of polyelectrolytes in highly concentrated aqueous solutions was characterized. We started to investigate concentrated aqueous solutions of sodium poly(styrenesulfonate) (NaPSS) and sodium poly(styrenesulfonate-*co*-maleic acid) (NaPSS-MA). The statistical copolymer of styrenesulfonate and maleic acid in a molar ratio of 3:1 was used as a component of significantly lower acidity. Furthermore, we were interested in the phase behavior of the ternary systems, in presence of the polycation PDADMAC. Phase diagrams for both polyanions were established, and samples from the "borderline" region as well as from the macroscopically homogeneous one phase region were investigated by means of polarized-light microscopy, freeze fracture electron microscopy, DSC and wide angle X-ray (WAXS) scattering.

2. Experimental

2.1. Materials

The polyelectrolytes were purchased by Aldrich. They were purified by ultrafiltration until the eluated solvent had a constant conductivity (usually about 70 μS/cm), and then characterized by gel permeation chromatography (GPC) in 0.5 N $NaNO_3$ solution. The results are given in Table 1.

2.2. Preparation

Different ways of mixing the components were tested, which showed no effect on the sample properties. Therefore the most accurate method, the mixing of the bulk polyelectrolytes by weight and then adding the water, was used for all further preparations. The samples were stirred and centrifuged several times until the sample was homogeneous (1ϕ) or separated into two phases (2ϕ). After one week the samples were analyzed again with regard to a macroscopic phase separation. Usually, the phase separation process starts immediately after stirring.

Macroscopically homogeneous samples from the 1ϕ-

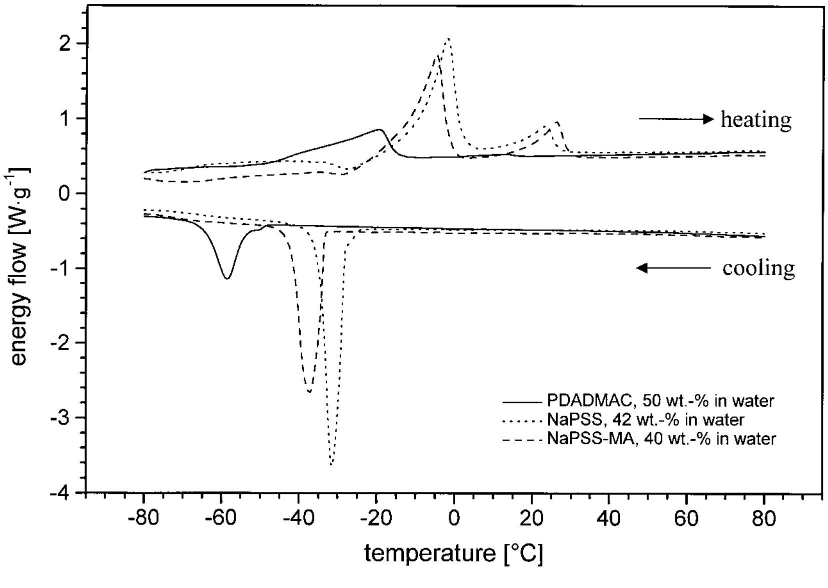

Fig. 1. Typical DSC curves for polyanion/water and polycation/water samples.

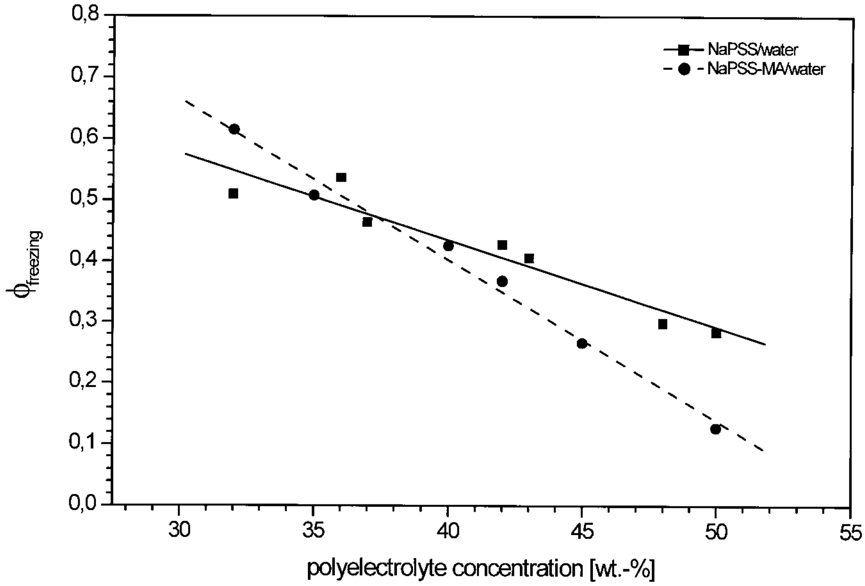

Fig. 2. Dependence of the free water on the polyelectrolyte content of the sample for the polyanion/water mixtures.

region were subjected to two different temperature programs:

1. “Cooling–heating-preparation”: Freezing up to −15°C, followed by heating up to +10°C ±5°C.
2. “Cooling–heating–cooling-preparation”: Freezing up to −15°C, followed by heating up to +30°C for about 30 seconds only and rapid cooling to +10°C ±5°C.

2.3. Methods

2.3.1. Polarized-light microscopy

The birefringence of the samples was detected by a Leica DMLB Microscope with crossed polarizers. The temperature program was adjusted with a peltier-element provided by Linkam Scientific Instruments.

2.3.2. Differential scanning calorimetry

The measurements were carried out with a Netzsch DSC-200 with a TA 414/3 controller unit, applying a temperature program from −80°C to +80°C and heating/cooling rate of 10 K/min. The second heating curve was always used to ensure the same thermal history for each sample.

2.3.3. Wide angle X-ray scattering

For the WAXS scattering an Enraf–Nonius PDS 120 powder diffractometer with a FR 590 generator was used. The samples were cooled during the examination with liquid nitrogen in a coolable sample holder TCU 100 from Paar Physica.

2.3.4. Electron microscopy

Fracturing and replication were carried out in a freeze fracture apparatus BAF 400 (Balzers, Liechtenstein), equipped with an electron beam evaporator. Etched preparations were obtained at −100°C after an etching time of 60 s before the Pt/C evaporation. The replicas were mounted on uncoated copper grids, and examined in an EM 902 (Zeiss, Germany).

Additionally, scanning electron microscopic investigations of the freeze etched samples were made with a cold field emission scanning electron microscope LEO 1530 (LEO Oberkochern, Germany)

3. Results and discussion

3.1. Binary polyelectrolyte/water systems

3.1.1. DSC-measurements

As shown in Fig. 1, concentrated aqueous solutions of

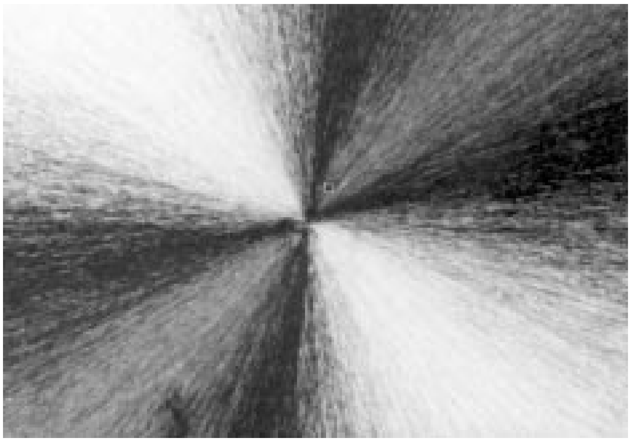

Fig. 3. Polarized-light microscopy image of the polyanion/water samples, showing the typical spherulitic texture of semicrystalline structures for polyelectrolyte contents between 20 and 50 wt%.

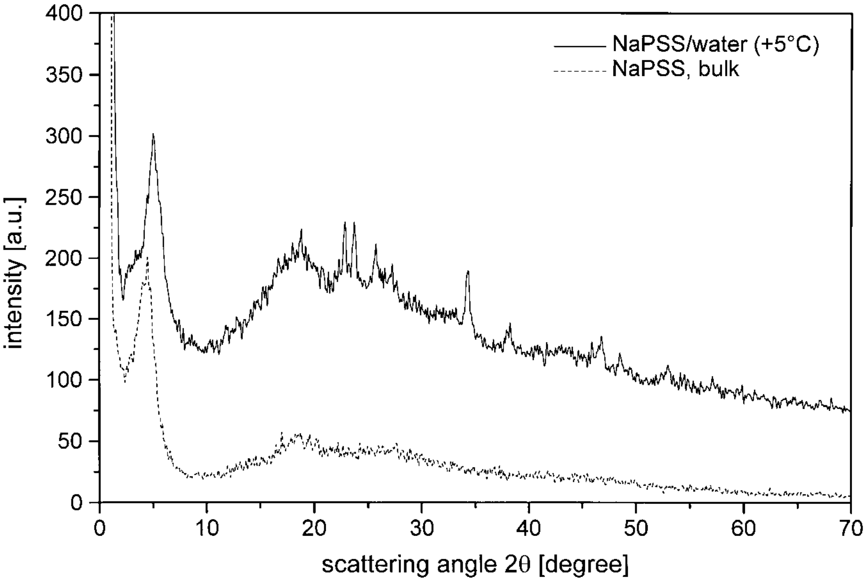

Fig. 4. WAXS diagrams for pure NaPSS and a concentrated NaPSS/water solution with a polyelectrolyte content of 42 wt%.

NaPSS and NaPSS-MA exhibit two endothermic peaks in the second heating curves, whereas the concentrated PDADMAC solution shows only one peak. The cooling curves of all systems have only one exothermic peak.

In all samples, the first peak in the heating curve at lower temperature is caused by the melting of free water in the sample, referred to as "freezing-water" [11]. This free water is not coordinated around the ionic groups of the polyelectrolyte. The amount of freezing water, ϕ_{freezing}, is proportional to the peak area of the corresponding peak from the DSC-curve, which equals the melting enthalpy ΔH_{l} of the freezing water. $\Delta H_{\mathrm{m,water}}$ is the melting enthalpy of pure water (334 J/g) and ϕ_{W} ($g_{\mathrm{water}}/g_{\mathrm{sample}}$) is the mass ratio of water of the sample:

$$\phi_{\mathrm{freezing}} = \frac{\Delta H_{\mathrm{l}}}{\phi_{\mathrm{W}} \cdot \Delta H_{\mathrm{m,water}}} \tag{1}$$

The amount of freezing water as a function of the polyelectrolyte concentration is given in Fig. 2. The amount of free water is reduced by increasing the PEL concentration, due to the fact that more and more water molecules are bound to the increasing number of ionic groups. In the case of the copolymer, the slope becomes steeper because

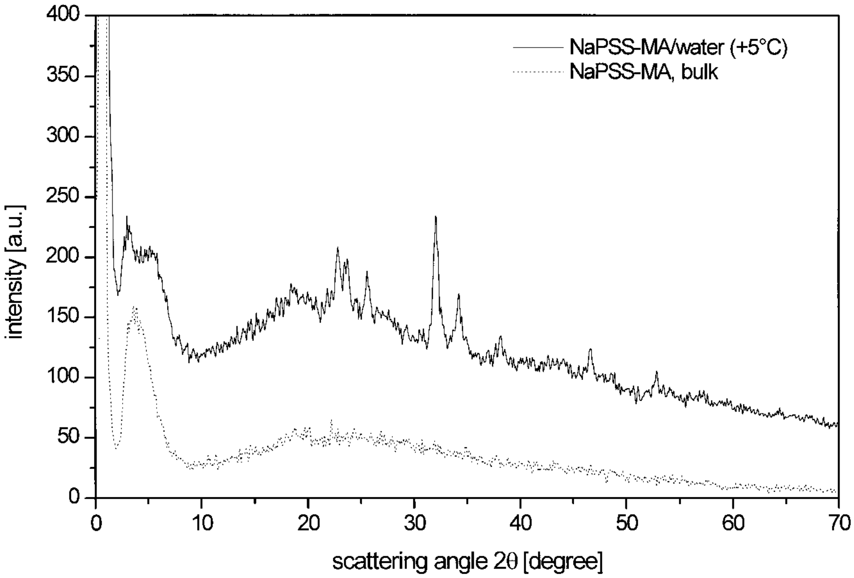

Fig. 5. WAXS diagrams for pure NaPSS-MA and a concentrated NaPSS-MA/water solution with a polyelectrolyte content of 40 wt%.

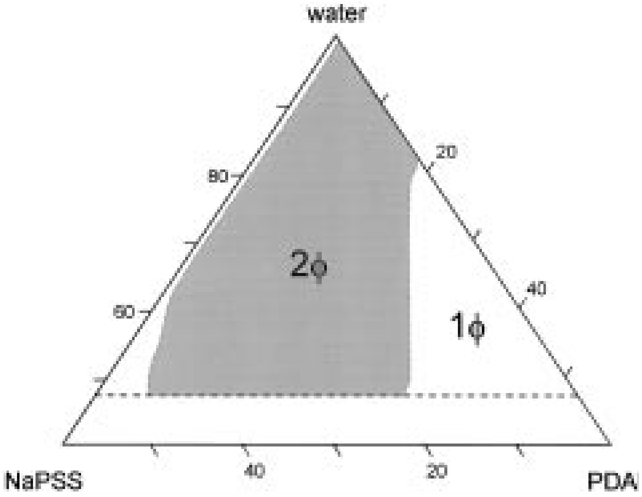

Fig. 6. Phase diagram of the NaPSS/PDADMAC/water system.

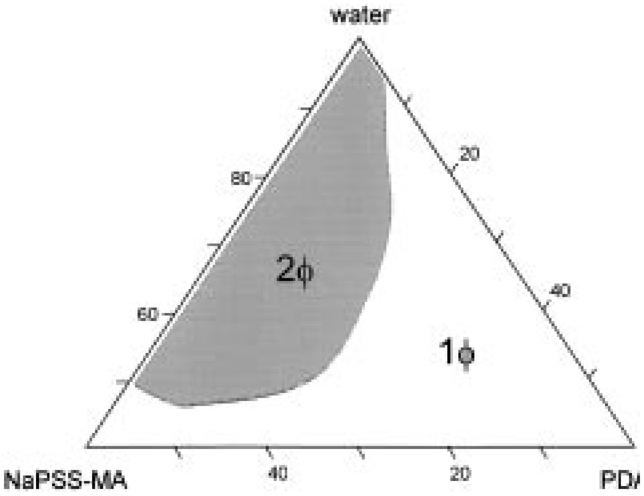

Fig. 7. Phase diagram of the NaPSS-MA/PDADMAC/water system.

of two ionic carboxylate groups at each monomer unit in contrast to only one sulfonate group. However deviations of the first peak from 0°C indicate that this peak is not exclusive really free water.

The second peak which occurs for the polyanion/water samples above 20°C can be attributed to the transition to the isotropic liquid state. It is caused by the "melting" of the spherulites found by polarized-light microscopy (see next paragraph). For the polycation PDADMAC alone no second peak could be found.

3.1.2. Polarized-light microscopy

The polarized-light microscopy shows optical patterns of spherulites for the polyanion/water systems after the "cooling–heating-preparation" in the temperature range between 0°C and 20°C (Fig. 3). The semicrystalline spherulites disappear by increasing the temperature above 20°C. That means that the second peak in the DSC-heating curve is caused by the "melting" of the microcrystallites.

In contrast to this, no textures in the polycation/water system could be observed.

3.1.3. Wide angle X-ray scattering

The bulk polyelectrolytes NaPSS, NaPSS-MA, PDADMAC show no crystalline reflexes (Figs. 4 and 5), whereas all investigated polyanion/water mixtures in the range between 30 to 70 wt% exhibit semicrystalline scattering patterns when the temperature was adjusted to +5°C after the "cooling–heating-preparation". An increase of the temperature leads to a drastic reduction of the scattering intensity. Typical scattering diagrams for NaPSS/water and NaPSS-MA/water mixtures are given in the Figs. 4 and 5 (after the "cooling–heating-preparation" at +5°C). The peaks are nearly independent of the type of polyanion, suggesting that the semicrystalline structure is induced by the styrenesulfonate units.

The peak positions are in agreement with those known from literature [12].

3.2. Ternary polyanion/polycation/water systems

3.2.1. Phase diagrams

The phase diagrams of the ternary systems NaPSS-MA/PDADMAC/water and NaPSS/PDADMAC/water are given in Figs. 6 and 7. In contrast to the NaPAA system [4] the range of phase separation is strongly increased by using the polyanion NaPSS. Thus, macroscopically homogeneous systems are observed only if one component is added in excess. By increasing the overall polymer concentration above 50 wt%, the "solution"-range is left and there is no longer a transition to a 1ϕ-region. The extent of the 2ϕ-region can be reduced significantly by replacing NaPSS by NaPSS-MA. In this case the borderline of the macroscopically homogeneous region becomes detectable over the whole range of

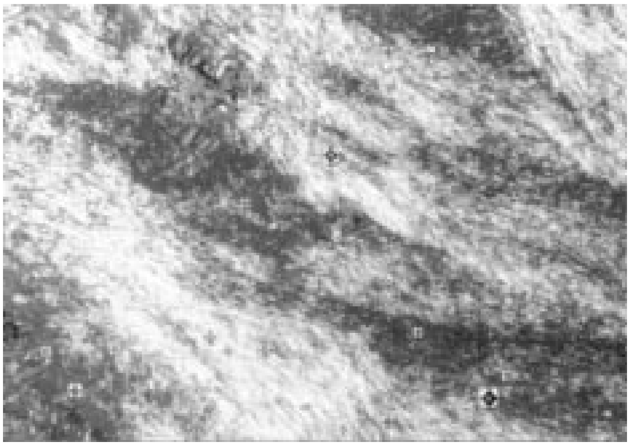

Fig. 8. Polarized (TEM) micrograph of sample HS_01 (see Table 2) from the NaPSS/PDADMAC/water system after the "cooling–heating-preparation".

Table 2
Results from the DSC measurements for selected polyanion/water and polycation/water systems

Sample name	Sample composition				1st peak of 2nd heating curve		2nd peak of 2nd heating curve	
	NaPSS (wt.%)	NaPSS-MA (wt.%)	PDADMAC (wt.%)	Water (wt.%)	Onset (°C)	Transition-enthalpy (J/g)	Onset (°C)	Transition-enthalpy (J/g)
	25			75	−3.5	150.8	2.0	61.2
	35			65	−4.9	109.4	10.6	72.8
	42			58	−8.3	92.6	15.1	87.1
		20		80	−3.1	212.0	13.7	6.0
		25		75	−4.3	179.9	14.8	10.7
		40		60	−13.7	94.5	19.0	28.2
HS_01	32		3	65	−19.1	42.6	17.8	19.7
HS_02	25		3	72	−13.0	89.6	15.7	16.4
CS_01		15	25	60	−18.8	85.2	14.8	10.9
CS_02		20	30	50	−29.6	47.3	28.7	16.2

composition. The composition of some characteristic mixtures taken from the one-phase region is given in Table 2.

3.2.2. Polarized-light microscopy

Highly concentrated NaPSS/PDADMAC/water mixtures of different compositions were taken from the one phase region of the phase diagram for observations of birefringence. It turned out that only weakly turbid samples taken from the borderline region between the one phase and the two phase regions show the characteristic "nebulous" textures of lamellar liquid crystalline structures after the "cooling–heating-preparation" (Fig. 8).

In the NaPSS-MA system, similar effects can be observed over a broader range of compositions (molar ratio of cationic to anionic functional groups). Fig. 9 shows a characteristic texture observed at 5°C after "cooling–heating-preparation".

By heating up the samples to +30°C, the textures under polarized light disappear, but when the mixture is then immediately cooled to a temperature of +5°C, after the texture has just disappeared ("cooling–heating–cooling-preparation"), we can observe a ordered "crystalline"-like textures. A typical example is given in Fig. 10 for the NaPSS/PDADMAC/water-system. When the samples were heated for a longer time, the textures could not be reestablished again.

Therefore polarized-light microscopy gives a hint at the transition from a semicrystalline state of the polyanion/water mixtures to a liquid crystalline state which appears upon adding the polycationic component PDADMAC. It has to be stated here that the temperature program as well as the temperature history of the sample are of great importance.

3.2.3. Differential scanning calorimetry

The investigated polyanion/polycation/water mixtures show two endothermic peaks in the second heating curves and again only one peak in the cooling curves (Figs. 11 and 12). The area of the first peak, which refers to the freezing water, decreases with increasing concentration of the polyelectrolytes. The enthalpy (ΔH_{tr}) of the second phase

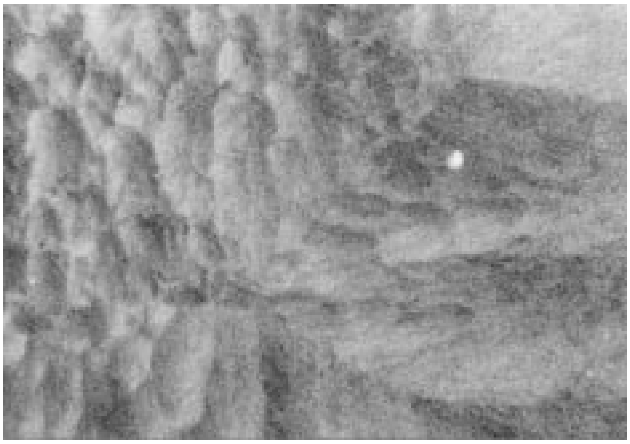

Fig. 9. Polarized (TEM) micrograph of sample CS_01 (see Table 2) from the NaPSS-MA/PDADMAC/water system after the "cooling–heating-preparation".

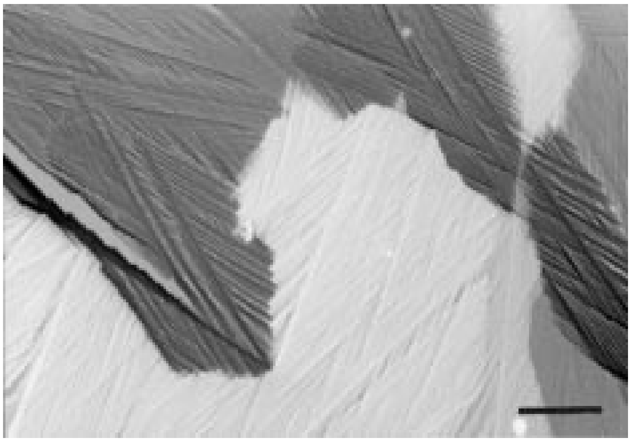

Fig. 10. Polarized (TEM) micrograph of sample HS_01 (see Table 2) from the NaPSS/PDADMAC/water system after the "cooling–heating–cooling-preparation" (scale bar: 200 μm).

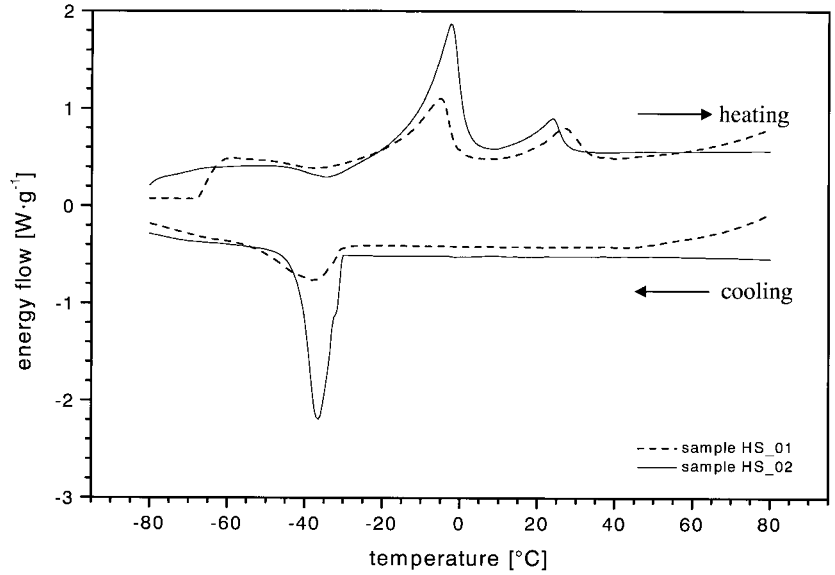

Fig. 11. DSC curve for two samples of the NaPSS/PDADMAC/water system.

transition changes significantly, when PDADMAC is incorporated into the polyanion/water system. In the system NaPSS/PDADMAC/water, ΔH_{tr} is reduced to 30% of the corresponding NaPSS/water system of corresponding concentration. Generally, ΔH_{tr} is decreased when NaPSS is substituted by NaPSS-MA (Table 2). However, by adding PDADMAC the opposite effect is observed.

The cooling curves of all investigated systems exhibit only one peak. This is of evidence for a slow reverse process belonging to the second transition.

3.2.4. Wide angle X-ray scattering

The observations from polarized-light microscopy and the results from the DSC investigations suggest that there may be a change from a crystalline to a liquid crystalline order when PDADMAC is added to the polyanion/water mixtures. To check this assumption, wide angle X-ray scattering was applied. The polyanion/polycation/water mixtures were investigated at +5°C after the "cooling–heating-preparation". By addition of PDADMAC, the Bragg-peaks disappear (Fig. 13), which means a loss of crystallinity. This reduction of the crystallinity is consistent with the change from a spherulitic to a liquid crystalline texture, as observed by polarized-light microscopy.

Unfortunately, the structures induced by the "cooling–heating–cooling-preparation" could not be characterized

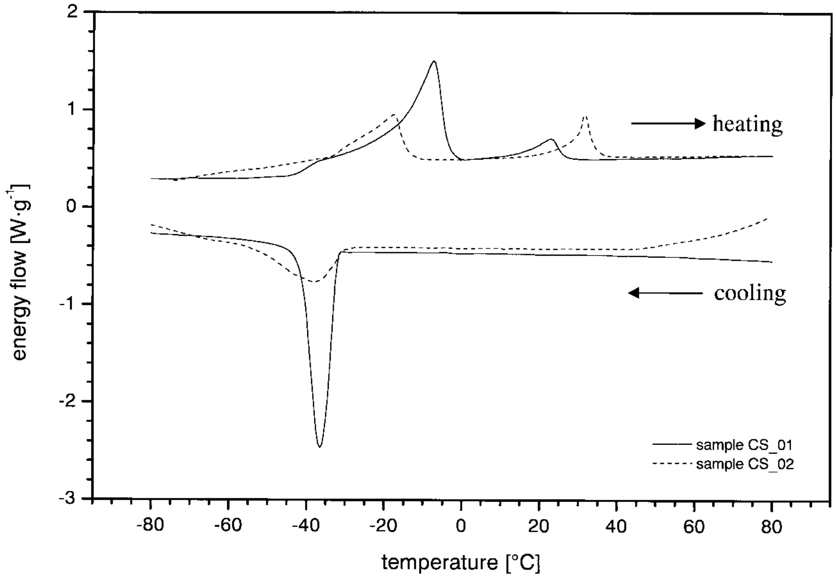

Fig. 12. DSC curve for two samples of the NaPSS-MA/PDADMAC/water system.

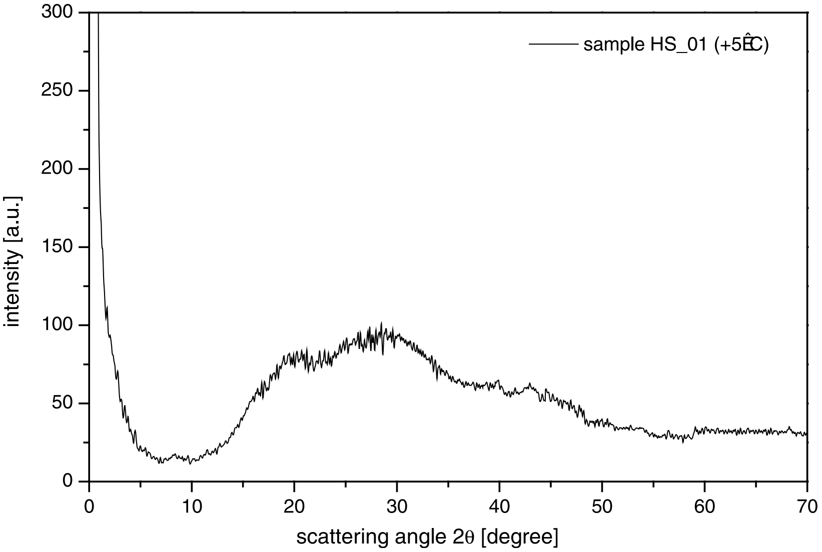

Fig. 13. WAXS diagram of sample HS_01 from the NaPSS/PDADMAC/water system.

by small angle X-ray scattering, since the cooling rates for the samples in the sample holder were not high enough, and so the destruction of the structure could not be avoided.

3.2.5. Electron microscopy

First of all, the weakly turbid NaPSS/PDADMAC/water mixture was characterized by cryo SEM microscopy. Fig. 14 shows spherical particles of about 0.5–1 μm in diameter, which can be assigned to spherical polyelectrolyte complex aggregates surrounded by the concentrated polyelectrolyte phase. These particles are responsible for the weak turbidity and should be needed as nuclei for the formation of the liquid crystalline phase. The freeze-fracture electron micrographs reveal a completely different morphology after the “cooling–heating-preparation”. Fig. 15 shows a “slate”-like structure, normally observed in lamellar liquid crystalline systems [13]. The “cooling–heating–cooling-preparation” induces the formation of a quite different supramolecular

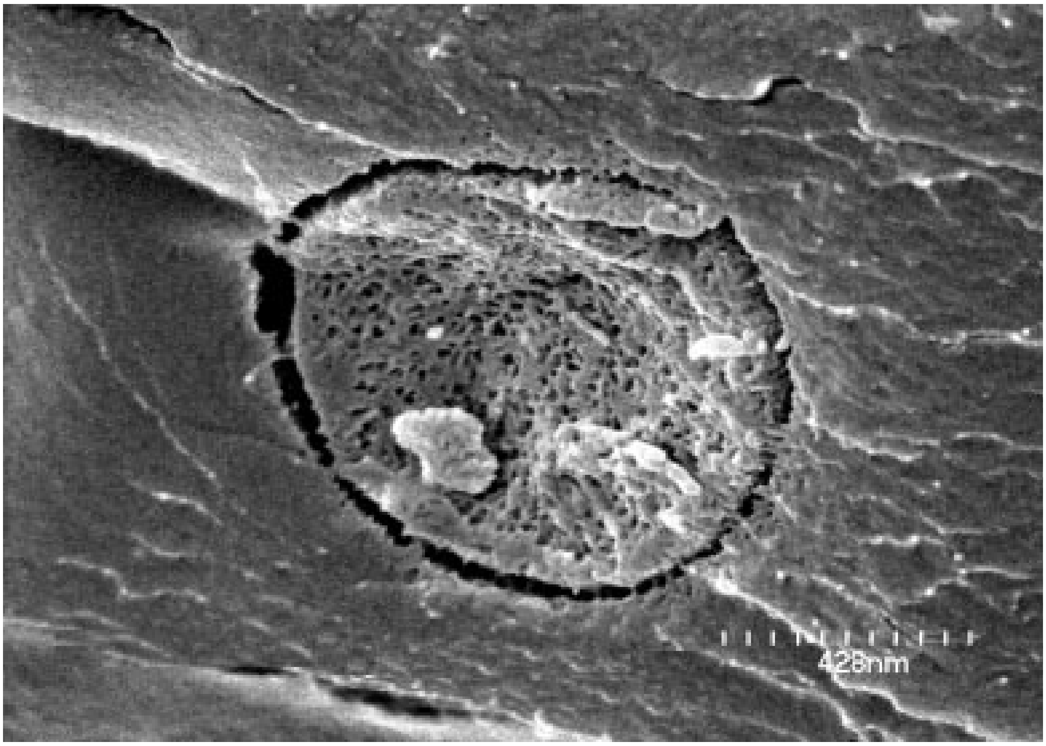

Fig. 14. Cryo-SEM image of sample HS_01 before applying a temperature program.

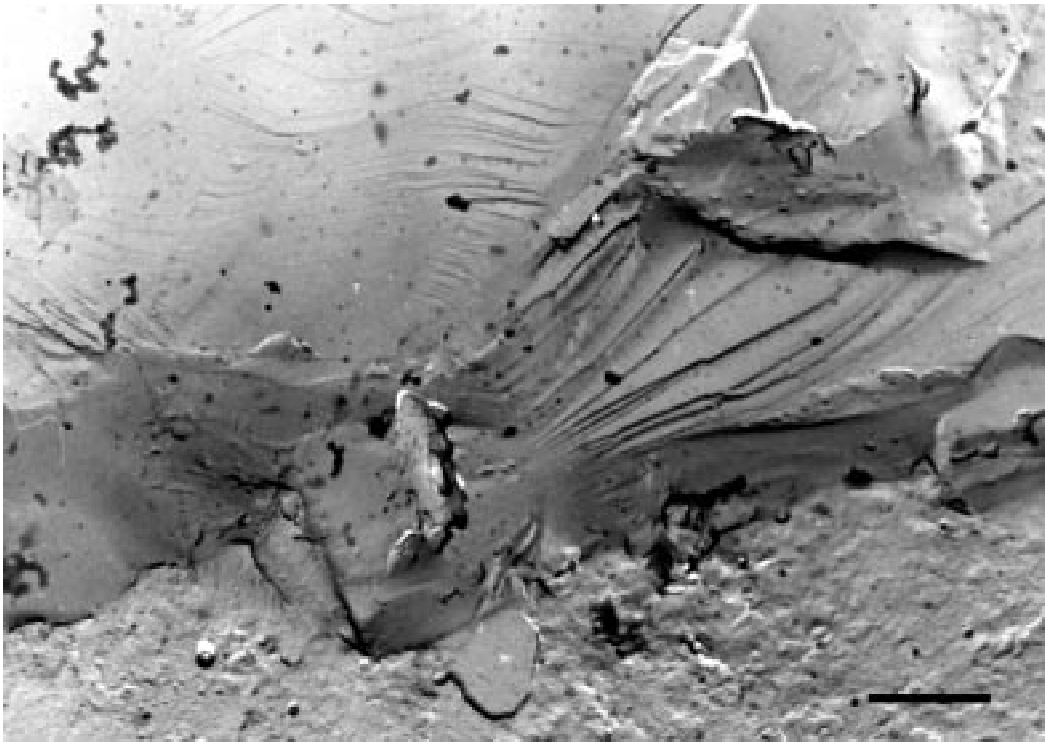

Fig. 15. TEM micrograph of sample HS_01 after the "cooling–heating–preparation" (scale bar: 1 μm).

structure. A characteristic picture is given in Fig. 16. The size of the observed individual "edges" (in the order of 1 μm) are in agreement with the size of a single "branch" found with polarized-light microscopy (compare to Fig. 10).

4. Conclusions

Concentrated aqueous NaPSS solutions form temperature sensitive semicrystalline structures in the temperature region

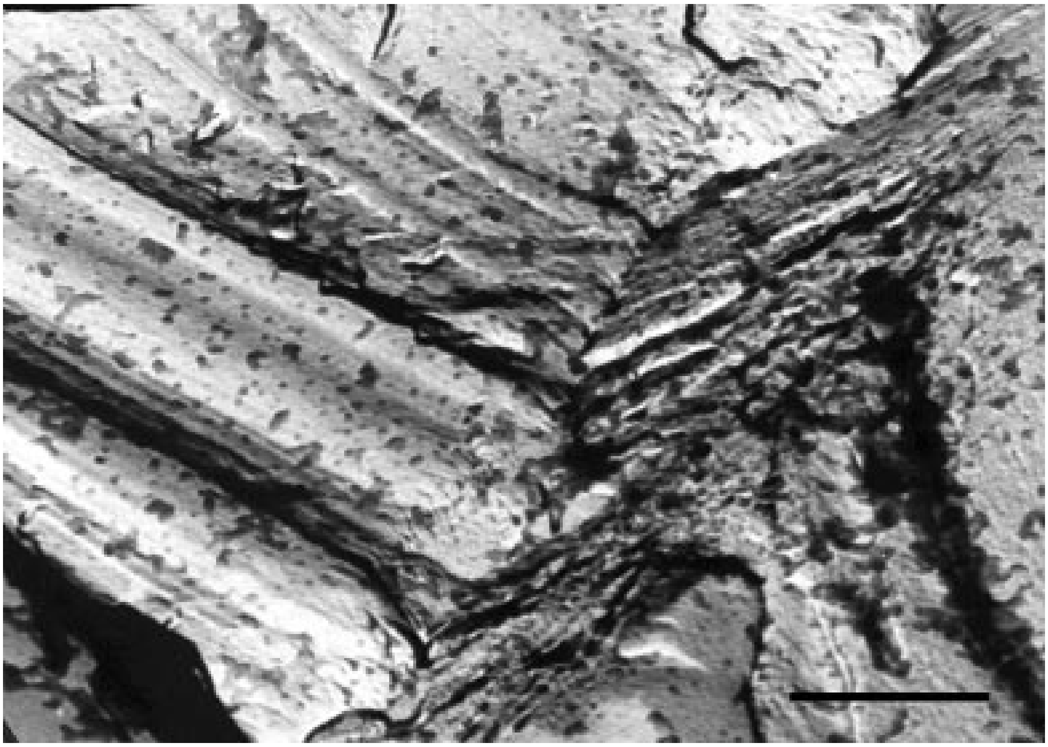

Fig. 16. TEM micrograph of sample HS_01 after the "cooling–heating–cooling-preparation" (scale bar: 1 μm).

from 0°C to 20°C as shown by spherulitic textures (polarized-light microscopy) and crystalline reflexes in WAXS. Copolymers with maleic acid show a similar semicrystalline behavior, which is induced by the styrenesulfonate-units.

Usually the addition of a polycation (PDADMAC) to aqueous polyanion systems induces a macroscopic phase separation due to the formation of polyelectrolyte complexes. The complex formation can be suppressed when an overall polyelectrolyte concentration, which depends upon the system, is attained. When the polyanion contains styrene sulfonic units (NaPSS, NaPSS-MA copolymer) this transition to a macroscopically homogeneous polyanion/polycation system can be observed above an overall polymer concentration of 30 wt%. Some of these mixtures show the typical optical pattern of lamellar liquid crystalline phases in the temperature region from about 0°C to 20°C. TEM-micrographs of the mixtures, freeze-etched at 5°C, show "slate"-like structures normally observed in lamellar liquid crystals. In contrast to the polyanion/water samples, the Bragg-peaks now disappear. These experimental facts can be explained by the formation of a liquid crystalline polyanion/polycation/water mixture. This means that the incorporation of the polycation decreases the semicrystalline order of the concentrated polyanion solution, and a liquid crystalline structure appears. A layer by layer assembly of the polyelectrolytes should be the reason for the assumed lamellar structure. For example polyelectrolytes and oppositely charged surfactants lead also to the formation of highly organized assemblies with lamellar structure [14].

Our observations given here opens a way to achieve to liquid crystalline "polyelectrolyte complexes". Nevertheless, the molecular weight and molecular weight distribution of the polymer components and temperature history of the samples is of great significance.

Acknowledgements

The financial support of the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. Markus Antonietti of the Max-Planck-Institute of Colloids and Interfaces for generous experimental support and Dr Brigitte Tiersch (University of Potsdam) for the electron microscopic investigations.

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