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Poly(ethylene imine) *n*-Alkyl Carboxylate Complexes

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Polyelectrolyte complexes of high-molecular-weight poly(ethylene imine) (PEI) and *n*-alkyl carboxylic acids were prepared. They were investigated with the use of differential thermal analysis, small- and wide-angle X-ray scattering techniques, and fluorescence spectroscopy. The chain lengths of the carboxylic acids varied from decanoic acid (C10) to hexacosanoic acid (C26). Order–order transitions from smectic C to smectic A structures were found, whose enthalpies increase with 3 kJ/mol per CH₂ group. The transitions result from the melting of *n*-alkyl side chains, which are packed into a two-dimensional hexagonal lattice. The transition temperatures, *T_m*, increased from –2 to 83 °C when the chain lengths were increased from C12 to C26. Thomson's rule was used to arrive at a quantitative description of the dependency of *T_m* on the chain length. Pyrene was incorporated into the complexes, and the apparent dielectric constant of its surroundings was determined to decrease stepwise with the increasing length of the side chains.

Introduction

Poly(ethylene imine) (PEI) is a branched, water-soluble polymer that is widely used in the paper industry.¹ At low pH values, PEI has the highest known charge density of all polyelectrolytes. A further characteristic of PEI is its high capability in forming a number of different complexes with metal ions,² anionic polyelectrolytes,^{3,4} and surfactants.⁵ Rabolt et al. have shown that PEI forms a strong polyion complex with monolayers of perfluorostearic acid.⁶ Such complexes are useful for making Langmuir–Blodgett films more robust. Kunitake et al. were able to prepare surfaces made of a PEI–surfactant complex which show an excellent blood compatibility.⁷ The optimization of PEI–DNA complexes as gene vectors with an excellent safety profile⁸ is another example of the numerous efforts being made in food, cosmetic, and pharmaceutical research to develop new applications for PEI. In an earlier study we reported on the complexation of PEI with retinoic acid, which serves as a possible new colloidal drug formulation.⁹

In this work, we report on complexes of high-molecular-weight PEI and carboxylic acids in the solid state. The

goal of this study is to understand the influence of the chain lengths of the carboxylate moieties on the thermal properties of the complexes and on the supramolecular structures.

Experimental Section

Materials. Water-free, high-molecular-weight poly(ethylene imine) (*M_w* = 25 000 g/mol) was supplied by BASF (Ludwigshafen, Germany). This polymer is highly branched, with molar ratios of 34:40:26 primary to secondary to tertiary amino groups). The carboxylic acids, pyrene and tetrahydrofuran (HPLC grade), were supplied by Aldrich and were used as received. The purity of the carboxylic acids was checked by determining their melting points and melt enthalpies using differential calorimetry. It was found that the melting points and the melt enthalpies are identical with the data reported in the literature.¹¹

Complex Preparation. For complex preparation, 22 mmol of PEI was dissolved in 20 mL of an ethanol–water mixture. The ratio of ethanol to water was 4:1 (v/v). Next, the PEI solution was slowly added to 11 mmol of the carboxylic acid, which was dissolved in 20 mL of hot ethanol (65 °C). The transparent solution was stirred for a further 30 min at 65 °C and then cast into films of the complex as described earlier.¹² Pyrene was incorporated into the complexes by dissolving the complexes in tetrahydrofuran and adding 0.05% (w/w) of pyrene. The homogeneous complex/pyrene solution was then cast into films.

Methods. The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer. The differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min^{–1} by applying two heating scans and one cooling scan. The onsets of the exothermic peaks in the second heating cycles were used to determine the melt transitions of the carboxylic acids and the PEI–carboxylate complexes. Wide-angle X-ray scattering (WAXS) measurements were carried out using a Nonius PDS120 powder diffractometer by transmission geometry. A FR590 generator was used as the source for Cu Kα radiation, monochromatization

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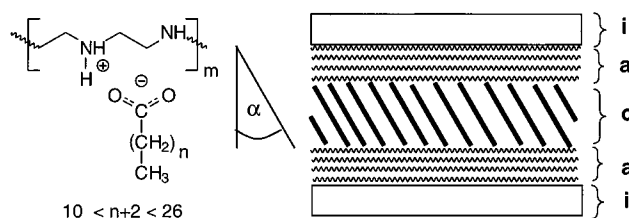


Figure 1. Molecular structure of the poly(ethylene imine) carboxylate complexes (left). The number of carbons of the carboxylates varies from 10 to 26. The sketch shows an idealized model of the partially crystalline lamellar structures of the complexes at temperatures below T_m : Ionic sheets are enriched in the protonated PEI chains and the carboxylic headgroups (i); the first 9 to 10 CH_2 groups of the carboxylate are disordered and located in (a); and the CH_2 groups beyond this limit are crystalline and located in (c). The average tilt angle, α , between the layer normals and the crystalline alkyl chains is about 40° .

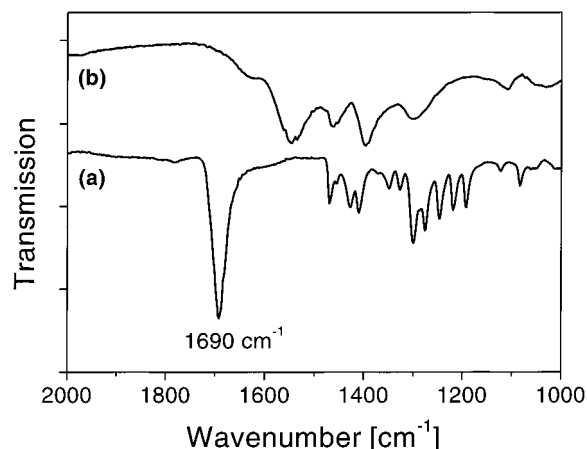


Figure 2. Infrared spectra of dodecanoic acid (a) and PEI-C12 (b). A strong carboxylic acid vibration band at 1690 cm^{-1} is present in the spectrum of the acid.

of the primary beam was achieved by means of a curved Ge crystal, and the scattered radiation was measured using a Nonius CPS120 position-sensitive detector. The resolution of this detector in 2θ was 0.018° . Small-angle X-ray scattering (SAXS) measurements were carried out using an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria, Model A-8054) equipped with image plates (type BAS III, Fuji). The image plates were read using a MAC Science Dip-Scanner (type IPR-420) and IP reader (type DIPR-420). The luminescence of complex films was analyzed using a Perkin-Elmer LS-50B luminescence spectrometer with front surface accessory. Emission spectra were collected in the range of 350 to 500 nm with an excitation wavelength of 330 nm and slits of 5/5 nm.

Results and Discussion

The molecular structure of the PEI-carboxylates is shown in Figure 1. The length of the chains of the carboxylate moieties in the complexes varies from 8 to 24 methylene groups, i.e., the acids contain 10 to 26 carbon atoms (PEI-C10 to PEI-C26) while the molecular weight of the PEI is constant ($M_w = 25\,000\text{ g/mol}$). We found that strong carboxylic acid vibration bands are present at 1690 cm^{-1} in the FTIR spectra of the pristine acids, although they are absent in the spectra of the corresponding PEI-carboxylate complexes. The FTIR spectra of dodecanoic acid and PEI-dodecanoate are shown as examples in parts a and b, respectively, of Figure 2. We conclude from the absence of the carboxylic acid vibration band that, within the experimental error, all of the acid functions form acid-base pairs. Therefore, the stoichiometry of ammonium to amino to carboxylate functions was 1:1:1 for all PEI-carboxylates.

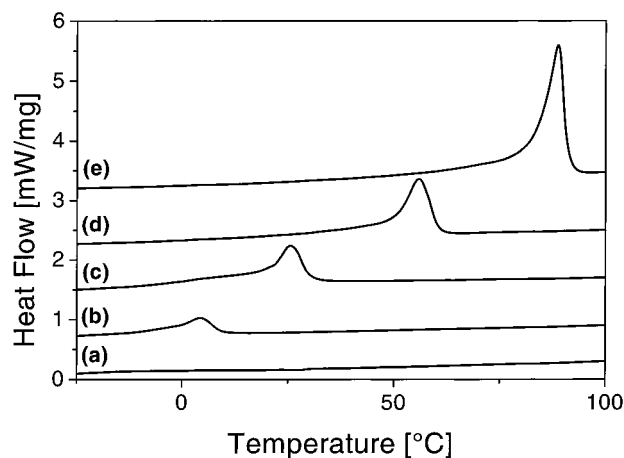


Figure 3. DSC traces of poly(ethylene imine) *n*-alkyl carboxylates: PEI-C10 (a), PEI-C12 (b), PEI-C14 (c), PEI-C18 (d), and PEI-C26 (e). Apart from PEI-C10, first-order transitions are present in the DSC traces of the complexes. The transition temperatures and transition enthalpies increase with increasing alkyl chain lengths.

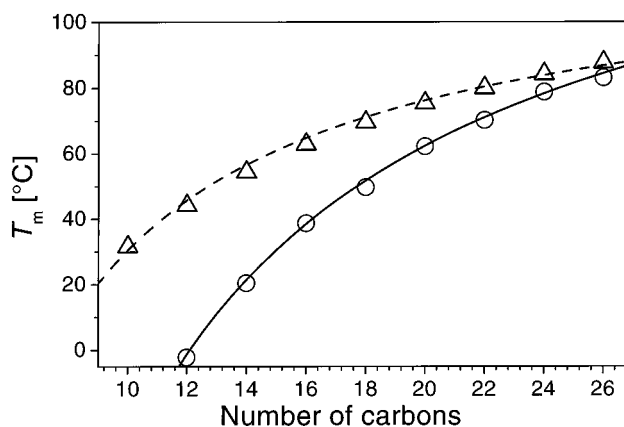


Figure 4. Melting points of the poly(ethylene imine) carboxylates (circles) and the pristine carboxylic acids (triangles). The dashed and the solid lines correspond to fit results according to eq 1 for the acids and the PEI-carboxylates, respectively.

Thermal Properties

The thermal properties of the complexes were investigated by using differential scanning calorimetry. We found that none of the complexes show a glass transition in the temperature range from -100 to 200°C . This probably is due to the high ionic character of the materials. In contrast to the absence of glass transitions, endothermic first-order transitions were found for the complexes PEI-C12 to PEI-C26. The temperatures of the transitions increase in the line from PEI-C12 (-2°C) to PEI-C26 (83°C). Only the complex with the shortest alkyl chain, PEI-C10, does not show an endothermic transition (see Figure 3). Tentatively, we assign these transitions to the melting of crystalline side chains which are formed from the tails of the carboxylate moieties. Examples of such crystallinity are the complexes of poly(L-lysine) and alkyl sulfates^{13,14} as well as poly(L-glutamates) with long *n*-alkyl side chains.¹⁵ In Figure 4 the melt transition temperatures, T_m , of the complexes and those of the noncomplexed carboxylic acids are plotted versus the number of carbons

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Table 1. Calorimetric Data for the Poly(ethylene imine)–Carboxylate Complexes: Melting Points (T_m), Melt Enthalpies (ΔH_m), and Number of Crystalline CH₂ Groups in the Side Chains (n_c)

| complex | T_m [°C] | ΔH_m [kJ/mol] | n_c |
|---------|------------|-----------------------|-------|
| PEI–C10 | | | 0 |
| PEI–C12 | –2.2 | 5.0 | 1.6 |
| PEI–C14 | 20.4 | 15.0 | 5.0 |
| PEI–C16 | 38.7 | 19.9 | 6.6 |
| PEI–C18 | 49.7 | 23.0 | 7.7 |
| PEI–C20 | 62.2 | 28.8 | 9.6 |
| PEI–C22 | 70.2 | 35.2 | 11.7 |
| PEI–C24 | 78.8 | 40.8 | 13.6 |
| PEI–C26 | 83.1 | 50.1 | 16.7 |

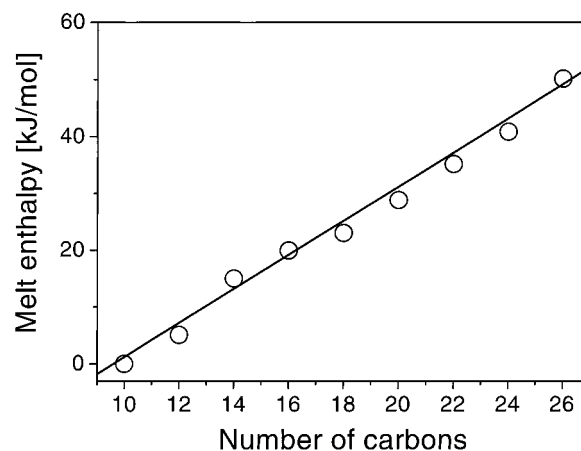
of the carboxylates and carboxylic acids, respectively. The figure shows that the increase in T_m with increasing chain length is much steeper for the complexes than for the pristine acids,¹¹ whereas the absolute values of T_m are lower for the complexes. For PEI–C12, the difference in the melt transitions between the pristine acid and the complex has the largest value (42 °C); for PEI–C26, it has the lowest value in the series of PEI–carboxylates (5 °C). We found that the shape of the curves in Figure 4 can be described by the expression

$$T_m = T_\infty \left(1 - \frac{c}{n}\right) \quad (1)$$

where T_∞ is the hypothetical melting point of a crystal with infinitely large side chains, c is a constant, and n is the number of carbon atoms of the carboxylate and the pristine acids, respectively. When we applied eq 1 to the measured data, we calculated T_∞ to be 157 ± 1 °C for the complexes and 122 ± 1 °C for the acids from the fit curves. The values for n are 12.1 ± 0.1 and 7.5 ± 0.1 . Equation 1 is equivalent to Thomson's rule, which describes the melting-point depression resulting from the finite size of crystallites in one direction.¹⁶ Such is the case, for example, for thin lamellar crystallites. In an earlier study we showed that PEI complexes with perfluorinated acids form lamellar structures consisting of stacks of alternating layers of ionic and nonionic sheets.¹⁷ Tentatively, we assume a structure for the PEI–carboxylates similar to that shown in Figure 1. The ionic sheets are enriched in protonated PEI chains and carboxylate headgroups. The nonionic sheets contain the alkyl chains, which are in an amorphous state for PEI–C10 and partially crystalline for the complexes with the longer chains. To estimate the degree of crystallinity, the melt enthalpies ΔH_m were determined. As expected, it was found that the melt enthalpies increase in the same line as the melt transition temperatures from PEI–C12 (5 kJ/mol) to PEI–C26 (50 kJ/mol). The quantities of the transition temperatures and the melt enthalpies are listed in Table 1. Figure 5 shows that the ΔH_m values fall on a line. Such linearity is usually observed in flexible main-chain polymers with the corresponding side-chain crystals¹⁵ and is represented by the equation¹⁸

$$\Delta H_m = n k + H_{m,e} \quad (2)$$

where k is the contribution of each added methylene group to the enthalpy and $H_{m,e}$ is a constant reflecting the contribution to the enthalpy due to the chain end. The value of k , evaluated from the solid line of Figure 5, is 3.0 ± 0.1 kJ/mol of methylene group; $\Delta H_{m,e}$ is -28.8 ± 2.6

**Figure 5.** Melt enthalpy of the complexes, dependent on the number of carbons that contain the carboxylate moieties (circles). The solid line is a linear fit with a slope of 3 kJ/mol of the CH₂ groups.

kJ/mol. The values of the noncomplexed carboxylic acids are $k = 4.2$ kJ/mol and $\Delta H_{m,e} = -14.6$ kJ/mol.¹⁹ We assume that the lower value of k results from a less-dense chain packing in the complexes as compared to the acids. It is known that the alkyl chains of 3-acyl-*sn*-glycerols are packed differently in the α - and β -phases: a densely packed triclinic subcell is formed in the β -phase with a melt enthalpy of 4.4 kJ/mol of methylene group. In the less densely packed β -phase with a hexagonal subcell of the alkyl chains, the melt enthalpy is 2.9 kJ/mol of methylene groups.²⁰ The latter value is close to that found for the PEI–carboxylate complexes. Therefore, we assume that the side chains form the less-dense subcell in the partially crystalline regions of the complexes. The numbers of crystalline CH₂ groups in a side chain, n_c , were calculated using the equation²¹

$$n_c = \frac{\Delta H_m}{k} \quad (3)$$

Table 1 shows that n_c increases from 0 (PEI–C10) to 16.7 (PEI–C26). Furthermore, it can be seen that n_c is equal to the number of carbons of the carboxylate moiety minus 9 to 10. From this we conclude that 9 to 10 methylene groups in the side chains are in a disordered, liquidlike state. Only the tails of the side chain extending beyond this limit participate in the crystallization. This result is in agreement with the work of Watanabe et al.,¹⁵ who found that the first 10 methylene groups in covalently bound side chains of poly(L-glutamate)s are in a disordered state and only the part beyond this limit crystallizes. Therefore, we conclude that the tendency of the side chains to crystallize is not significantly affected by the type of bonding, either covalent or ionic, between the side chains and the polymeric backbone.

Supramolecular Structures. Wide- and small-angle X-ray measurements were undertaken in order to reveal the molecular and supramolecular structures of the complexes. Examples of wide-angle diagrams of the complexes and the pristine acids are given in Figure 6. It

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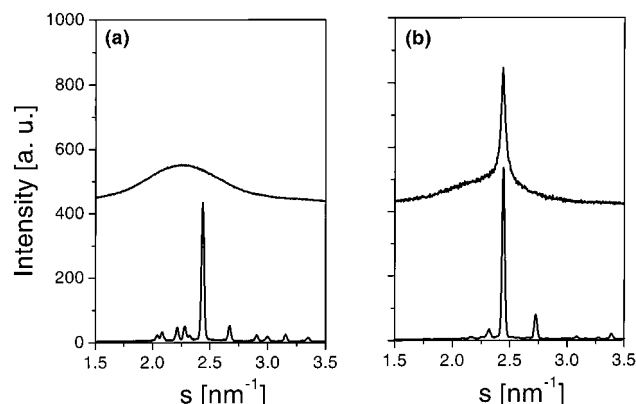


Figure 6. Wide-angle X-ray scattering diagrams of *n*-decanoic acid (a, lower curve), PEI-C10 (a, upper curve), *n*-octadecanoic acid (b, lower curve), and PEI-C18 (b, upper curve). The scattering vector is defined as $s = 2/\lambda \sin \theta$.

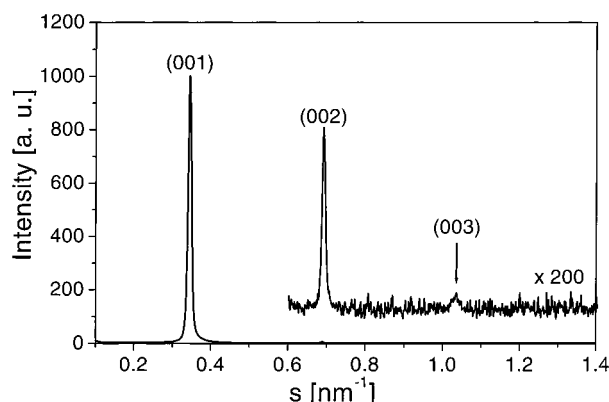


Figure 7. Small-angle X-ray scattering curve of PEI-C12 with equidistant reflections. At higher scattering vectors, the intensity of the curve is magnified by a factor of 200.

was found in the wide-angle diagrams of the complexes that only a broad maximum with a Bragg spacing of 0.45 nm is present at temperatures higher than the melt transition temperatures as determined by DSC. This finding is consistent with a liquidlike ordering of the alkyl chains in the complexes below T_m . At temperatures lower than T_m , an additional reflection with a Bragg spacing of 0.41 nm was found in the wide-angle scattering diagrams of the complexes. The intensity of this reflection increases with increasing chain length, consistent with the proposed side-chain crystallinity at temperatures below T_m . A comparison of the wide-angle diagrams of the complexes and the noncomplexed acids reveals that the alkyl chains in the complexes are less densely packed than those in the acids. The partially crystallized side chains in the complexes are nonspecifically packed in a two-dimensional hexagonal lattice with a chain-to-chain distance of 0.47 nm, whereas the chains in the carboxylic acid are three-dimensionally, specifically, and tightly packed.²² The conclusion of the lower packing order of the side chains in the complexes confirms the results from differential calorimetry. In the small-angle scattering diagrams of all the complexes, two or three reflections with equidistant positions are present. An example is shown in Figure 7. As expected, the positions of the maxima shift to smaller scattering vectors in the line from PEI-C10 (2.60 nm), PEI-C12 (2.89 nm), PEI-C14 (3.13 nm), PEI-C16 (3.31 nm), PEI-C18 (3.42 nm), PEI-C20 (3.44 nm), PEI-C22

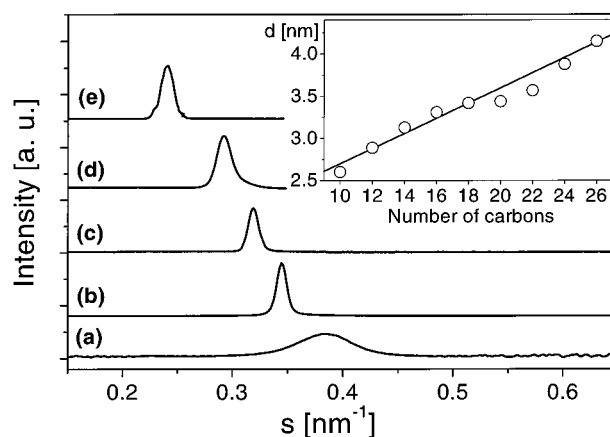


Figure 8. Small-angle X-ray scattering curves of PEI-C10 (a), PEI-C12 (b), PEI-C14 (c), PEI-C18 (d), and PEI-C26 (e) in the region of the first-order reflection. The inset shows the long period d versus the number of carbon atoms of the carboxylates (circles) and a linear fit (solid line).

(3.57 nm), and PEI-C24 (3.88 nm) to PEI-C26 (see Figure 8). In contrast to the wide-angle scattering diagrams, the small-angle diagrams of the complexes do not differ significantly at temperatures below and above T_m . Only the widths of the reflections increase slightly with temperature. This result, together with the results from the thermal analysis and the wide-angle scattering measurements, led us to conclude that the structures of the complexes are smectic C at temperatures below T_m and smectic A above T_m . The increase in the layer distance is not strictly linear (see Figure 8, inset). Such a phenomenon was first reported by Antonietti et al. in a series of polystyrenesulfonate *n*-alkyl trimethylammonium complexes.¹² Their complexes were lamellar-structured but varying in the curvature of the lamellae, i.e., the lamellae are undulated. For higher chain lengths the undulations are periodical, which leads to additional reflections in the small-angle scattering curves. In contrast to the polystyrenesulfonate complexes, no additional reflections were present in the scattering diagrams of the PEI-carboxylate complexes. Therefore, nonperiodic undulations of the layer surfaces can be present within the structure of the complexes. This is a possible explanation for the deviation of the linear increase in the long period. But periodic undulations of the lamellae obviously can be ruled out. If the possibility of the presence of undulations as a structural detail is ignored, a linear extrapolation of the increase of the layer distance gives an increment of 0.09 ± 0.01 nm per CH_2 group and an interpolated value of 1.8 ± 0.2 nm for $n = 0$ (see Figure 8, inset). Then the crystalline alkyl chains are interdigitated and have an average tilt angle (α) of about 40° with respect to the normals of the layers (see Figure 1). The next question is, are ordered supramolecular structures possible in view of the branching of the PEI? Chen and Hsiao have reported on lamellar complexes with dodecylbenzenesulfonic acid for the same PEI with $M_w = 25\,000$ g/mol and ratios of primary to secondary to tertiary amino groups of 34:40:26.²³ They showed that considerable branching does not hinder the formation of an ordered supramolecular complex structure. Further, Hwang and Kim have shown that PEI of the same molecular weight and degree of branching could be very effective in assembling rigid Langmuir-Blodgett monolayers of fatty acids.²⁴ Therefore, the occurrence of self-assembled structures with a high

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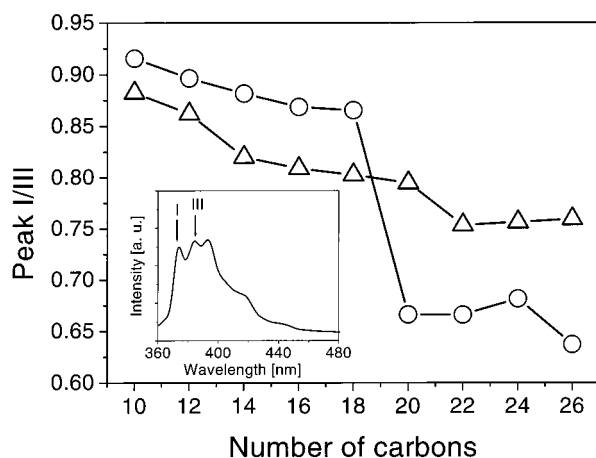


Figure 9. Plot of I_I/I_{III} for the emission of pyrene incorporated in the complexes (circles) and in the pristine acids (triangles) as a function of the number of carbons of the carboxylates and the acids, respectively. The inset shows a typical fluorescence spectrum of pyrene when incorporated in a complex (PEI-C12). The spectrum is dominated by the monomer spectrum which shows a characteristic vibration fine structure with clearly separated bands I and III. The pyrene concentration was 0.05% (w/w).

degree of order is not inconsistent with an irregular structure of the polymer backbone of PEI.

Incorporation of Pyrene. Pyrene was incorporated into the complexes as a typical hydrophobic compound. To obtain information on how the pyrene is located in the lamellar structures, we carried out steady-state fluorescence measurements on pyrene-doped films of the complexes. The $\pi \rightarrow \pi^*$ emission spectrum of monomer pyrene exhibits five major vibronic bands between 370 and 400 nm, labeled I...V in progressive order. A typical example of a pyrene-doped film spectrum is shown in Figure 9 (inset). The vibration bands I, at 372.4 nm, and III, at 382.9 nm, are clearly resolved. It is known that peak I shows a significant decrease in its intensity compared with peak III when the polarity of the surroundings of the pyrene decreases. Thus the ratio of the emission intensities of the vibronic bands I and III (I_I/I_{III}) serves as a measure of the polarity of the pyrene's surroundings. For example, the I_I/I_{III} ratio is 0.58 in hexane and 1.87 in water.²⁷ Dipole-induced dipole interactions (Ham effect) between pyrene and its microenvironment are responsible for the changes of the intensity ratio I_I/I_{III} .^{25,26,28} The I_I/I_{III} ratio of the complexes and the pristine acids as a function of the number of carbon atoms is plotted in Figure 9 (circles and triangles, respectively). The I_I/I_{III} ratio for both the complexes and the acids decreases with increasing chain length. This result is in agreement with the picture that the surroundings of the pyrene become more and more nonpolar with an increasing alkyl chain length. However, the decrease for the acids as a matrix for pyrene is more or less continuous and reduces from $I_I/I_{III} = 0.88$ (C10) to

0.76 (C26). By contrast, the absolute value of I_I/I_{III} is higher for the complexes with the shorter alkyl chains. It decreases from 0.92 to 0.87 in the line from PEI-C10 to PEI-C18. This means that the surroundings of the pyrene in these complexes are more polar than in the corresponding acids, but for PEI-C20 to PEI-C26 this tendency is reversed: the surroundings of the pyrene are less polar in the complexes than in the corresponding acids. The sharp step in the decrease of I_I/I_{III} from PEI-C18 to PEI-C20 is surprising. For comparison, the relative intensities of I_I/I_{III} of pyrene in a number of solvents were introduced as the Py scale of the solvent polarities.^{27,28} There is no theoretical understanding of the solvent sensitivity of I_I/I_{III} , for example, in terms of the dielectric constant (ϵ) of the solvent. Nevertheless, the I_I/I_{III} values provide insights into the effective polarity within individual microdomains.²⁸ For the complex with the shortest alkyl chain length (PEI-C10), the local surroundings of the pyrene ($I_I/I_{III} = 0.92$) are close to those of pyrene that is dissolved in *n*-octanoic acid ($I_I/I_{III} = 0.91$, $\epsilon = 2.85$). The decrease of the I_I/I_{III} ratio from PEI-C10 to PEI-C18 is only a small one, so the effective polarity of pyrene can be considered constant. The effective polarity of the surroundings in the line from PEI-C20 to PEI-C26 also can be considered almost constant. The ratio is close to that of pyrene that is dissolved in hexadecane ($I_I/I_{III} = 0.60$, $\epsilon = 2.04$). From the low I_I/I_{III} values in all complexes, it can be concluded that the pyrene is exclusively incorporated in the nonionic layers which contain the alkylated chains. Further, a possible explanation for the steplike decrease of the I_I/I_{III} ratio from PEI-C18 to PEI-C20 is the formation of highly nonpolar cavities in the crystallites of the side chains. The minimum number of crystalline carbon atoms in the side chains instrumental in forming such a cavity seems to be 10. We assume that the pristine acids are not able to form the same cavities because their alkyl chains are more densely packed than those in the complexes.

Conclusion

We have demonstrated that the complexation of poly(ethylene imine) with *n*-alkyl carboxylic acids results in ionic complexes with lamellar structures. The complexes show order-order transitions from smectic C to smectic A, and the transition temperatures increase with the increasing lengths of the alkyl chains. The first 9 to 10 CH₂ groups within all the structures are disordered, whereas beyond this limit they are arranged in a two-dimensional hexagonal lattice. The dependency of the phase transitions on the lengths of the side chains can be described by Thomson's rule, and the increase in the phase-transition enthalpies is about 3 kJ/mol per CH₂ group. Fluorescence measurements using pyrene as a dopant of the complexes show that the pyrene is homogeneously incorporated into the structure of the complexes and that the polarity of its surroundings is sensitively influenced by the chain lengths of the carboxylate moieties.

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