Lamellar architecture and crystalline transformation in supramolecular complexes of highly-branched polyethyleneimine-octadecanoic acid†

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Supramolecular complexes of PEI(OA)$_x$ show a lamellar structure, and reversible crystal phase transition of the side alkyl chains in the complex can be observed by temperature-variable FT-IR spectroscopy.

The supramolecules of polymer–amphiphile complexes can be self-assembled into structural patterns of various length scales through a delicate balance of association interactions and repulsive interactions. In recent years, the mesomorphic structures of such complexes have been studied extensively and a variety of structures have been revealed.[1] Most reports in this area are related to the lamellar morphology which consists of alternating polymer and amphiphile layers.[2] The crystalline phase of the lamellae is mainly composed of alkyl chains of the amphiphiles, among which protrusion interactions may lead to phase transformation. Luyten and co-workers found that both hexagonal (α_H) and orthorhombic (β_O) packing of alkyl chains can occur in the complexes of poly(4-vinylpyridine)pentadecylphenol with different compositions.[3] Our earlier studies also indicated that the dynamic equilibrium of the polymer-amphiphile complex affects the phase stuctures in an essential way, which could alter the ordered packing of the alkyl chains in the complexes.[4] Such investigations also revealed the self-assembled mesomorphic structure in the complexes, especially in highly-branched polymer–amphiphile complexes and amphiphilic dendrimers.[5]

In such highly-branched polymer–amphiphile complex systems in the solid state, to the best of our knowledge, neither the regularity of the microstructure variations with composition, nor the dynamic transition of the crystalline phase with temperature has been reported before. The aim of this study is to understand the influence of the content of amphiphile moieties on the supramolecular architecture as well as the mechanism of the temperature-induced isomorphic crystalline phase transitions of alkyl chains, in the complexes of highly-branched polyethyleneimine-octadecanoic acid (PEI(OA)$_x$, where x denotes the average numbers of OA per ethyleneimine repeat unit; x = 0.60, 0.76, 0.96, 1.03, 1.13, or 1.67).

A series of PEI(OA)$_x$ were synthesized through the interfacial reaction of PEI aqueous solution with OA–carbon tetrachloride solution (ESI†).

Thermal properties of the complexes were examined using differential scanning calorimetry (DSC). After quenching from the molten state, the DSC traces of PEI(OA)$_{0.60}$ and PEI(OA)$_{0.76}$ exhibited glass transitions (Tg) at about 19 °C and 28 °C, respectively, corresponding to the amorphous domains in the two complex systems. As x exceeds 1.0, however, Tg could not be detected, probably due to the high ionic character of the materials with a higher content of OA. The melting temperatures for the PEI(OA)$_x$ complexes showed an increasing trend from 54.48 °C to 68.42 °C in the range of x = 0.60–1.03, then a decreasing trend from 68.42 °C to 66.04 °C as x becomes larger than 1.03 (Fig. S1, ESI†). These transitions are tentatively assigned to the melting of crystalline side chains formed from the tails of the carboxylate moieties.[6] The increase

of the transition enthalpies indicates that the side alkyl chains form more regular crystalline phases as the OA content increases (x = 0.60–1.03). On the contrary, the decrease of the transition enthalpies in the range of x = 1.13–1.67 is probably due to the co-crystallization effect of the dissociative OA with the side alkyl chains of the complex, which led to less compact stacking of crystalline region.[7]

As mentioned above, both hexagonal (α_H) and orthorhombic (β_O) packing of side alkyl chains may occur in polyelectrolyte–surfactant complexes with different compositions. In the present study, temperature variable FT-IR spectra of pure OA and PEI(OA)$_{1.03}$ were investigated, respectively (Fig. 1). The results shown in Figs. 1a, 1b obviously indicate that both α_H and β_O packing of alkyl chains coexist in pure OA over the whole temperature range of the study, with predomination of α_H packing at higher temperatures and β_O packing at lower temperatures, corresponding to the relative variation of I_{730}/I_{720}.[8] The vibrational behavior of the side chains in PEI(OA)$_{1.03}$ (Figs. 1c, 1d), however, is quite different from those of pure OA. As the temperature is lowered below 0 °C, the bands at 720 cm^{-1} and 730 cm^{-1} can be detected separately, though I_{730}/I_{720} is much smaller than that of pure OA (mainly β_O packing of alkyl chains occurs), suggesting the coexistence of α_H and β_O packing. When the temperature is higher than 0 °C, only one peak at 720 cm^{-1} was observed in the range of 740–700 cm^{-1}. Even the peak-resolve procedure could not detect the existence of β_O packing. Such phenomena appeared for both the heating and cooling processes, and were easily reduplicated as the sample was circulated to be heated or cooled. This reversible phase transformation of the PEI(OA)$_x$ complexes promises a potential application as a temperature activated reversible switch.
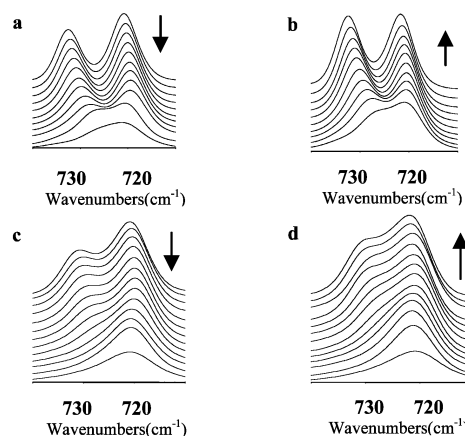

Fig. 1 Temperature-variable FT-IR spectra of pure OA and PEI(OA)$_{1.03}$. (a) Heating process of OA, from top to bottom: −125, −100, −80, −60, −40, −20, 0, 20, 40, 60, 75 °C, respectively; (b) cooling process of OA, from bottom to top: 60, 40, 20, 0, −20, −40, −60, −77, −100, −121 °C, respectively; (c) heating process of PEI(OA)$_{1.03}$, from top to bottom: −163, −136, −120, −100, −80, −60, −40, −20, 0, 20, 40, 60, 77 °C, respectively; (d) cooling process of PEI(OA)$_{1.03}$, from bottom to top: 77, 56, 38, 15, 0, −20, −40, −60, −80, −100, −120, −140, −160 °C, respectively.

The reversible crystalline phase transformation of the side alkyl chains in the complex has resulted from the rearrangement of OA molecules in the crystalline region. As the temperature increases, some of the carboxyl groups of OA start to associate with amine groups of PEI through proton transfer or hydrogen bonding, leading to association of OA–amine groups or the formation of hydrogen bonding "dimers". This association is reversible as temperature decreases.[9] This is to say, that the reversible crystalline phase transformation is controlled by the hydrogen bonding balance between the interaction of amine–carboxyl groups and carboxyl–carboxyl groups in the PEI–OA complexes. The reason why only hexagonal crystalline form occurs at higher temperatures is still not clear.

Fig. 2 displays the SAXS profiles of the complexes at room temperature. With lower OA content in $PEI(OA)_x$, *i.e.*, $x \leq 1.03$, SAXS profiles showed only one scattering peak at about $2\theta = 1.48$–$1.52°$, implying a unique ordered structure in the complexes. The scattering intensity is most intensive for $PEI(OA)_{1.03}$, indicating that as the ratio of OA to EI unit is around 1, the complex has the most ordered structure. This result indicates that the highly-branched characteristic of PEI does not hinder the formation of an ordered supramolecular complex structure, as was proven before.[10] A second scattering peak occurred as $x \geq 1.13$, which is probably due to the existence of another crystalline structure of dissociated OA in the complexes, with a corresponding long period of about 40 Å.
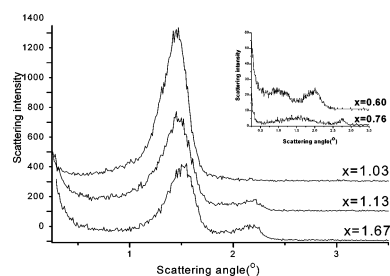

Fig. 2 SAXS profiles of $PEI(OA)_x$ complexes at room temperature.

According to Strobl and Schneider,[11] we can calculate the thickness of amorphous layers (La) and crystalline layers (Lc), and then infer a packing model of the alkyl side chains (Table 1 and Fig. 3). With the increase of the OA content, the packing model of side alkyl chains transforms from entirely inter-digitated (Fig. 3a) to end-to-end bimolecular layers (Fig. 3c), with a partially interdigitated model in the transient state (Fig. 3b, 3d). Table 1 indicates that the long period increases with the increase of the OA content in the range of $x = 0.60$–1.03, which can be explained by the increase of repulsive interactions with the increase of the OA content. As x is larger than 1.03, however, the long period decreases with the increase of the OA content, which may be a consequence of the incorporation of dissociated OA into the crystalline lattice of the side alkyl chain and results in a better packing.[7] Due to this better packing from co-crystallization, the long period decreases by approximately 4–6 Å to 58–56 Å. This implies that the mesoscopic dimensions can be tuned by varying the OA content. Regardless of the OA content, the thickness of the amorphous layers (PEI and polar

Table 1 Thickness of the crystalline layer and the amorphous layer of side alkyl chains, calculated from SAXS results (Fig. S2 ESI†)

Sample	L/Å	La/Å	Lc/Å	Packing model
$PEI(OA)_{0.60}$	42.26	23.0	19.26	Entirely interdigitate
$PEI(OA)_{0.76}$	46.48	23.0	23.48	Partially interdigitate
$PEI(OA)_{1.03}$	62.50	25.5	37.00	End to end model
$PEI(OA)_{1.13}$	58.85	24.5	34.35	Partially interdigitate
$PEI(OA)_{1.67}$	56.21	23.5	32.71	Partially interdigitate

a.$PEI(OA)_{X\ll1.0}$ b. $PEI(OA)_{X<1.0}$

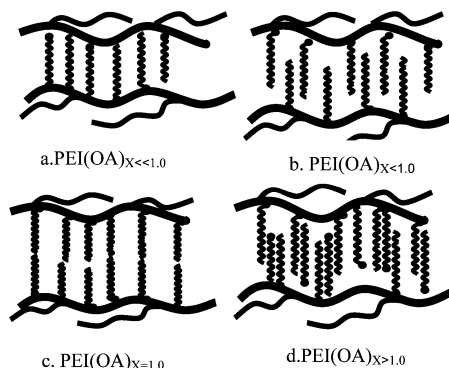c. $PEI(OA)_{X=1.0}$ d.$PEI(OA)_{X>1.0}$

Fig. 3 Schematic presentation for the layer structure of $PEI(OA)_x$.

carboxylic head group) keeps a constant of *ca.* 23–25.5 Å, implying the variation in long period stemmed from the swelling of the crystalline layer. Similar results were obtained by Schenning and coworkers with XRD and cryo-TEM methods.[5c] It was found that polypropyleneimine-palmitoyl chloride dendrimers display clear periodicities for different generations.

In order to confirm the SAXS results, TEM experiments were carried out to characterize the lamellar structure of $PEI(OA)_x$ complexes. The imaging for $PEI(OA)_{1.03}$ and $PEI(OA)_{1.13}$ clearly showed the well-ordered lamellar structures with repeated lamellar distances of approximately 60.8 Å and 50.9 Å, respectively (Fig. S3†), in good agreement with the SAXS results (62.5 Å and 58.85 Å, respectively). The consistency between the SAXS and TEM results gives the validity of the model we have proposed above.

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