Phase modulation of thermotropic liquid crystals of tetra-n-alkylammonium polyoxometalate ionic complexes

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A series of composition analogous polyoxometalate-based ionic complexes are synthesized and studied, with a focus on the correlation between their mesomorphic behavior and their chemical structure. Generally, these polarizable rigid polyoxoanion clusters decorated with hydrophobic flexible alkyl chains have demonstrated a propensity to form thermotropic liquid-crystalline (LC) phases. Characterized by differential scanning calorimetry (DSC), polarized optical microscopy (PM), and X-ray diffraction (XRD), two of the four investigated complexes tend to form thermodynamically stable mesophases. Longer alkyl chains have been found to form mesophases, and the alkyl chain length of the quaternary ammonium cations influences both the occurrence and type of mesophase exhibited.

1 Introduction

Hybrid inorganic–organic complexes are one of the most potentially significant fields of investigation in contemporary materials chemistry. Among the variety of routes used for the preparation of these hybrid materials, supramolecular self-assembly, as a controllable technique at the nanosized level, is providing promising perspectives through weak intermolecular forces (i.e. van der Waals forces, hydrogen bonds, electrostatic forces). The properties of the inorganic and organic species should be maintained in the complex, and eventually new desired properties could also be obtained.

Polyoxometalates (POMs), a class of discrete, negatively charged early transition metal oxide clusters, possess a wealth of topologies and physical and chemical properties. The anionic character of a POM cluster allows its incorporation into materials possessing cationic groups to yield various inorganic–organic hybrid materials. Among the obtained hybrid materials containing POMs, the most commonly used cations are the tetraalkylammonium and tetraalkylphosphonium cations, and the properties of the material can be tailored by adjusting the composition and ratio of the cations and the polyoxoanions. For example, functional POM-containing LB films and multilayers were fabricated, in which tetraalkylammonium cations were used as the structure-directing agents. Introducing mesogenic units into the alkyl chain of the tetraalkylammonium cations to encapsulate POMs could lead to the formation of liquid crystal hybrid materials. The POM-based ionic liquids were obtained by pairing the size and charge of the cation with the polyoxoanion.

In a prior report, we presented a new class of POM-based ionic liquid crystal materials without mesogenic units. In this system, hydrophilic POM clusters and hydrophobic tetra-n-octylammonium cations formed ionic amphiphiles. Despite the fact that neither the POMs nor the tetra-n-octylammonium cations are mesogens, the ionic interaction and polar–apolar incompatibility force the microsegregation responsible for the mesomorphism of these complexes. This result prompted us to extend our investigations, we are very interested in the impact on the nature of the complex due to a change in the length of the alkyl chain of the quaternary ammonium cation. Moreover, studying the self-assembly behavior and the structure property relationship of the POM-based ionic complexes is essential for the exploration of further applications. Hence, a series of tetra-n-alkylammonium POM complexes have been prepared by a straightforward ion exchange reaction in this study. These complexes have a fixed Keggin-type polyoxoanion SiW12O404−, containing different chain lengths of tetraalkylammonium cations ([((CnH2n+1)4N]+, n = 4, 6, 8, 10). The properties of these materials have been investigated by Fourier Transform (FT) IR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), optical polarizing microscopy (PM), and X-ray diffraction (XRD).
2 Experimental section

2.1 Materials

All chemicals were obtained commercially and used without additional purification. H₄SiW₁₂O₄₀ was freshly prepared according to the procedure described in the literature.⁵ All other reagents were readily available from commercial sources and used as received without further purification.

2.2 Synthesis

This series of complexes \([([C_{n}H_{2n+1}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}, \; n = 4, 6, 8, 10)\), a type of zwiterion, were produced through a slightly modified reaction. For example, in the synthesis of \([([C_{8}H_{17}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}\), an aqueous solution of H₄SiW₁₂O₄₀ was dropped into a hot aqueous solution of tetra-\(n\)-octylammonium \((n\text{-Oct}_{4}N^+\) salt under vigorous stirring, and the molar ratio of SiW₁₂O₄₀⁻ to \(n\text{-Oct}_{4}N^+\) was controlled at 1:4. After stirring for 1 hour at room temperature, a white precipitate was obtained by filtration. The precipitate was washed with distilled water several times, and dried in a vacuum desiccator until the weight remained constant. Other samples were synthesized following a similar procedure. The obtained complexes are abbreviated as 4-SiW, 6-SiW, 8-SiW and 10-SiW, respectively.

4-SiW: Anal. calcld for 4-SiW \((C_{64}H_{144}N_{4}O_{40}\text{SiW}_{12}, 3843.9966)\): C, 37.02; H, 6.52; N, 1.08. Found: C, 36.80; H, 6.42; N, 1.16. TGA suggests 4-SiW is thermally stable up to ca. 340 °C and no significant loss of weight occurs below this temperature. A mass loss of ~25% from 340 °C to 470 °C is attributed to the gradual decomposition of the organic cations. Combining the results of EA and TGA, 4-SiW should correspond to the tentative formula: \([([C_{4}H_{9}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}\).

6-SiW: Anal. calcld for 6-SiW \((C_{96}H_{208}N_{4}O_{40}\text{SiW}_{12}, 4292.8472)\): C, 26.86; H, 4.88; N, 1.31. Found: C, 26.86; H, 4.85; N, 1.27. TGA suggests 6-SiW is thermally stable up to ca. 260 °C and no significant loss of weight occurs below this temperature. A mass loss of ~33% from 260 °C to 450 °C is attributed to the gradual decomposition of the organic cations. Combining the results of EA and TGA, 6-SiW should correspond to the tentative formula: \([([C_{6}H_{13}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}\).

8-SiW: Anal. calcld for 8-SiW \((C_{128}H_{272}N_{4}O_{40}\text{SiW}_{12}, 4741.6977)\): C, 32.42; H, 5.78; N, 1.18. Found: C, 32.81; H, 5.74; N, 1.16. TGA suggests 8-SiW is thermally stable up to ca. 220 °C and no significant loss of weight occurs below this temperature. A mass loss of ~40% from 220 °C to 430 °C is attributed to the gradual decomposition of the organic cations. Combining the results of EA and TGA, 8-SiW should correspond to the tentative formula: \([([C_{8}H_{17}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}\).

10-SiW: Anal. calcld for 10-SiW \((C_{160}H_{336}N_{4}O_{40}\text{SiW}_{12}, 5190.5483)\): C, 37.02; H, 6.52; N, 1.08. Found: C, 36.80; H, 6.42; N, 1.00. TGA suggests 10-SiW is thermally stable up to ca. 220 °C and no significant loss of weight occurs below this temperature. A mass loss of ~45% from 220 °C to 420 °C is attributed to the gradual decomposition of the organic cations. Combining the results of EA and TGA, 10-SiW should correspond to the tentative formula: \([([C_{10}H_{21}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}\).

2.3 Physical characterization

The IR spectra in KBr pellets were recorded in the range 400–4000 cm⁻¹ with an Alpha Centaurt FT/IR spectrophotometer. Elemental analysis (C, H, N) was performed on a Flash EA1112 from Thermo Quest Italia SPA. Thermal properties of the samples were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurements were performed on a TA DSC Q20 instrument at a scanning rate for both heating and cooling of 5 °C min⁻¹ for 8-SiW and 10-SiW and 10 °C min⁻¹ for 4-SiW and 6-SiW. The samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen. TGA was carried out using a TA SDT-Q600 instrument, with a heating rate of 10 °C min⁻¹, under a nitrogen atmosphere. The texture of the samples was observed using an Axioskop 40 polarizing microscope (Carl Zeiss Light Microscopy, Germany) equipped with a LINKAM THMS 600 hot stage and a LINKAM CI 94 temperature controller. For variable-temperature XRD measurements, a Bruker AXS D8 ADVANCE X-ray diffractometer using Cu Kα radiation with a wavelength of 0.154 nm with an mri Physikalische Geräte GmbH TC-Basic temperature chamber was used.

3 Results and discussion

3.1 Synthesis

To prepare these tetra-\(n\)-alkylammonium POM complexes, two different methods can be adopted. The first method involves the direct reaction of the POM with tetra-\(n\)-alkylammonium bromide in aqueous solution to produce the desired product. In the second method, a solution of tetra-\(n\)-alkylammonium bromide in chloroform or dichloromethane is dropped into an aqueous solution of POM with vigorous stirring and this can also produce tetraalkylammonium POM salts. The second method has been used more for the preparation of complexes containing longer alkyl chains (such as DODA). In our experiments, tetra-\(n\)-alkylammonium bromide was dissolved in water when heat was applied, to avoid the difficulty of separation in the experiment. Therefore, the first method was used for the preparation of \([([C_{n}H_{2n+1}]_{4}N]_{4}\text{SiW}_{12}\text{O}_{40}, \; n = 4, 6, 8, 10)\).

3.2 FTIR spectroscopy studies

All four samples have been investigated by FTIR spectroscopy, and the detailed assignments of the bands are summarized in Table 1. From the FTIR spectroscopy, we can see that all ionic complexes are formed from tetra-\(n\)-alkylammonium cations and Keggin polyoxoanions.

Infrared spectroscopy is an effective measurement for alkyl chain systems study. Fig. 1 shows the FTIR spectra of samples in the high frequency region and in the low frequency region, respectively. In the high frequency region, the bands at around 2962 ± 10 cm⁻¹ and 2872 ± 10 cm⁻¹ are assigned to antisymmetric (\(\text{r}^–\)) and symmetric (\(\text{r}^r\)) stretching vibrations of the terminal methyl groups, respectively. We can evaluate the rotational freedom of the chain terminus from the splitting of the \(\text{r}^r\) mode. The splitting indicates the decreasing symmetry.
of the CH$_3$ group as a result of the intermolecular interactions between the alkyl chains. A single peak in our samples shows that the CH$_3$ group should be in at least a C$_3$ symmetry. For the CH$_2$ modes, their antisymmetric (d$^-$) and symmetric (d$^+$) values are at around 2926 ± 10 cm$^{-1}$ and 2853 ± 10 cm$^{-1}$ respectively. A shift in the d$^-$ and d$^+$ frequencies of the CH$_3$ is a helpful tool to study the order of the alkyl chains in the complexes: low frequencies (2918 and 2850 cm$^{-1}$) of the bands are characteristic of a highly ordered chain, while their upwards shift is indicative of a conformational disorder increase. On the basis of this rule, the observed frequencies of our complexes, the $\nu_{as}$(CH$_3$) and $\nu_{s}$(CH$_3$) shift to higher frequencies, implying the presence of highly disordered alkyl chains in the complexes. In addition, the disordered conformer of the sample becomes less favoured with an increasing alkyl chain length. The wavenumber for $\nu_{as}$(CH$_2$) decreases from 2935 cm$^{-1}$ to 2924 cm$^{-1}$, and the wavenumber for $\nu_{s}$(CH$_3$) decreases from 2862 cm$^{-1}$ to 2853 cm$^{-1}$. This result can be explained by the fact that the increasing van der Waals interactions in the longer chains lead to an increase in the order of the alkyl chain arrangement. In addition, the intensity ratio $I_{s}$(CH$_2$)/$I_{as}$(CH$_3$) has often been used as an indicator of the alkyl chain arrangement. The conformational order of the alkyl chain increases with an increase in the frequency ratio $I_{2853}/I_{2925}$. The inset of Fig. 1 shows a plot of $I_{s}$(CH$_2$)/$I_{as}$(CH$_3$) versus the number of CH$_2$ groups. It can be seen that the ratio increases with an increase in the length of the alkyl chains, implying that the conformational order increases, which can be regarded as a result of the interactions between the alkyl chains increasing with the increase in chain length.

In the low frequency region, the absorption bands are mostly composed of the scissoring, wagging, twisting and rocking modes of the CH$_2$ group and the stretching mode of the polyoxyanion SiW$_{12}$O$_{40}$$. The slightly split peaks at ~1483 and ~1467 cm$^{-1}$ are associated with the CH$_2$ scissoring bending modes, which are widely used to investigate the packing arrangement of alkyl chains. The appearance of a single narrow peak at ~1483 cm$^{-1}$ is attributed to the triclinic packing of the alkyl chains, and the single narrow band at ~1467 cm$^{-1}$ corresponds to hexagonal packing. The appearance of a well-resolved doublet with two distinct components is known to either derive from the intermolecular vibrational coupling due to the crystal-field splitting in the orthorhombic/ monoclinic packing or from the coexistence of triclinic and hexagonal packing in the solid state. In the present case, the less resolved doublet is possibly derived from the latter because the packing of the alkyl chains is not close, as can be elucidated by their frequencies in the high wavenumber region. Compared with the band at ~1483 cm$^{-1}$, the increasing intensity of the band at ~1467 cm$^{-1}$ indicates an increasing tendency towards the alkyl hexagonal packing arrangement. The order of the packing arrangement increases.

### Table 1: The assignment of the vibration modes in the IR spectra of the complexes

<table>
<thead>
<tr>
<th>Samples</th>
<th>4-SiW</th>
<th>6-SiW</th>
<th>8-SiW</th>
<th>10-SiW</th>
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<td>2926</td>
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<td>$\nu_{as}$(CH$_3$)</td>
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<tr>
<td>2859</td>
<td>2859</td>
<td>2855</td>
<td>2853</td>
<td>$\nu_{s}$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1484</td>
<td>1483</td>
<td>1482(w)</td>
<td>1481(w)</td>
<td>$\delta$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1466(w)</td>
<td>1468</td>
<td>1468</td>
<td>1467</td>
<td>$\delta$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1381</td>
<td>1379</td>
<td>1378</td>
<td>1378</td>
<td>$\delta$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1014</td>
<td>1010</td>
<td>1010</td>
<td>1010</td>
<td>$\nu$(C–C)</td>
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<td>967</td>
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<td>968</td>
<td>967</td>
<td>$\nu$(W–O$_a$)</td>
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<td>920</td>
<td>920</td>
<td>$\nu$(Si–O$_c$)</td>
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<td>$\nu$(W–O$_c$–W)</td>
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<td>723</td>
<td>723</td>
<td>$\rho$(CH$_3$)</td>
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$^a$ as, antisymmetric; s, symmetric; $\nu$, stretching; $\delta$, scissoring; $\rho$, rocking.

### Fig. 1: The high frequency region of the FTIR spectra of the complexes (left); the low frequency region of the FTIR spectra of the complexes (right). Inset: the plot of $I_{s}$(CH$_2$)/$I_{as}$(CH$_3$) versus the number of CH$_2$ groups.
with an increase in the chain length, which is consistent with the increasing order of the alkyl chains in the high frequency region. The band at ~1377 cm\(^{-1}\) corresponds to the CH\(_3\) scissoring bending modes. The polyoxoanion SiW\(_{12}\)O\(_{40}\)\(^4-\) shows four characteristic absorption bands about at 969, 920, 883 and 799 cm\(^{-1}\) due to the W–O\(_s\), Si–O\(_p\), W–O\(_b\)–W and W–O\(_c\)–W vibrations, respectively. In addition, the band at ~721 cm\(^{-1}\) is assigned to the in-plane rocking (\(\rho\)) mode of methylene with more than four consecutive CH\(_2\) groups.

### 3.3 Thermal studies

The thermal properties of these materials were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis. TGA curves for representative samples under a nitrogen atmosphere are shown in Fig. 2. Decomposition temperatures, taken from the onset of weight loss, are listed in Table 2. It should be noted that these are dynamic data, static decomposition temperatures may be considerably lower.\(^{32}\) In the present case, the TGA traces of the samples showing weight loss are observed above 340 °C for 4-SiW and the decomposition temperatures of 6-SiW, 8-SiW and 10-SiW are about 260 °C, 220 °C and 220 °C, respectively.

![Thermal gravimetric curves of 4-SiW, 6-SiW, 8-SiW and 10-SiW.](image-url)

**Fig. 2** Thermal gravimetric curves of 4-SiW, 6-SiW, 8-SiW and 10-SiW.

### Table 2 Transition temperatures and enthalpies of the transition and decomposition temperature of the samples from the DSC thermograms

<table>
<thead>
<tr>
<th>Samples</th>
<th>Transition</th>
<th>First cooling</th>
<th>Second heating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(T_f) (°C)</td>
<td>(\Delta H) (J g(^{-1}))</td>
</tr>
<tr>
<td>4-SiW(^a)</td>
<td>Cr1-Cr2</td>
<td>260.0</td>
<td>9.369</td>
</tr>
<tr>
<td>6-SiW(^a)</td>
<td>Cr1-Cr2</td>
<td>139.6</td>
<td>5.710</td>
</tr>
<tr>
<td>8-SiW(^b)</td>
<td>Cr1-Cr2</td>
<td>36.3</td>
<td>2.693</td>
</tr>
<tr>
<td>8-SiW(^b)</td>
<td>Cr2-X</td>
<td>86.4</td>
<td>1.869</td>
</tr>
<tr>
<td>10-SiW(^b)</td>
<td>Cr1-X</td>
<td>112.6</td>
<td>3.049</td>
</tr>
<tr>
<td>10-SiW(^b)</td>
<td>X-I</td>
<td>6.3</td>
<td>4.529</td>
</tr>
<tr>
<td>10-SiW(^b)</td>
<td>X-I</td>
<td>173.8</td>
<td>2.322</td>
</tr>
</tbody>
</table>

\(^a\) Scanning rate of 10 °C min\(^{-1}\); \(^b\) scanning rate of 5 °C min\(^{-1}\); \(T_f\): peak temperature; Cr: crystalline; X: mesophases; I: isotropic, \(T_d\): decomposition temperature.

The DSC curves are shown in Fig. 3. The transition temperatures and enthalpies obtained from the DSC thermograms are gathered in Table 2. DSC analyses showed that all samples exhibit reversible thermal transitions. In general, the transition temperatures are significantly influenced by the alkyl chain length. Comparing the complexes in this series, it can be seen that a change in the length of the alkyl chains causes the difference in the phase transition. The results show that there is a reversible phase transition before the decomposition of 4-SiW and 6-SiW. The DSC curve of 8-SiW shows the presence of three reversible phase transition peaks. For 10-SiW, there exists two reversible phase transition processes.

8-SiW and 10-SiW were investigated using polarized optical microscopy (PM). Upon heating, 8-SiW and 10-SiW behave in different ways. 8-SiW begins melting at around 90 °C and gradually becomes a highly viscous fluid. On approaching 135 °C, the viscosity of the sample drops and it can free flow. Upon cooling from this temperature, a visible texture is observed until about 90 °C. Then the sample gradually crystallizes with the decrease in temperature. Fig. 4 shows these results, which can be detected using PM upon cooling from the isotropic liquid state. 10-SiW melts directly into an isotropic liquid at around 180 °C. On cooling, at around 170 °C, the sample becomes a highly viscous fluid and it is difficult to spread with the application of mechanical strain. The sample did not show obvious birefringence and no obvious texture was observed. After leaving the sample at room temperature for about 1 hour, crystallization is observed. It is difficult to identify the type of mesophase from the PM pictures directly. The textures of 8-SiW and 10-SiW are not representative due to the absence of classic mesogenic units in the complexes.

### 3.4 Powder X-ray diffraction

X-ray diffraction was used to verify the existence of a liquid crystalline phase and to confirm the nature of the phase observed from DSC and PM. Data are collected on cooling from the isotropic phase and Fig. 5 shows the X-ray diffraction pattern of these complexes.

The XRD of 4-SiW at 30 °C (Fig. 5(a)) shows several reflections which are assigned as (111), (200), (220), (310) and (222) from the good fit of the linear plot of 1/\(d_{hkl}\) versus \((h^2 + k^2 + l^2)^{1/2}\). This XRD pattern agrees with the pattern of the micellar cubic phase with a \(Pm3m\) lattice or the bicontinuous cubic phase with a \(Pn3m\) lattice.\(^{13,14}\) The lattice parameter is calculated to be 22.5 Å using the following equation: \(a = (2^{1/2}d_{111} + 4^{1/2}d_{200} + 8^{1/2}d_{220} + 10^{1/2}d_{310} + 12^{1/2}d_{222})/5\). The number of molecules in a unit cell (Z) is calculated to be ca. 4 from \(Z = (a^3N_A)/M\), where \(N_A\) is Avogadro’s number (6.02 × 10\(^{23}\) mol\(^{-1}\)).
and $M$ is the molecular weight (3844.0 g mol$^{-1}$). The density ($\rho$) of the complex is about 2.29 g cm$^{-3}$, which has been determined by a flotation method.\textsuperscript{34,35}

The XRD of 6-SiW at 190 °C (Fig. 5(b)) shows several reflections which are assigned as (110), (200), (211), (220) and (222) from the good fit of the linear plot of $1/d_{hkl}$ versus $(h^2 + k^2 + l^2)^{1/2}$ for the observed diffraction peaks.\textsuperscript{34} This XRD pattern agrees with the pattern of the micellar cubic phase with an $Im\overline{3}m$ lattice. The lattice parameter is calculated to be 21.35 Å using the following equation: $a = (2^{1/2}d_{110} + 4^{1/2}d_{200} + 6^{1/2}d_{222}$

Fig. 3 DSC curves of (a) 4-SiW, (b) 6-SiW, (c) 8-SiW and (d) 10-SiW.

Fig. 4 PM images of 8-SiW at (a) 90 °C, (b) 70 °C and (c) 32 °C, and 10-SiW at (d) 120 °C, (e) 38 °C, and (f) after leaving at room temperature for about 1 hour during the cooling process (magnification: x100).
The number of molecules in a unit cell \((Z)\) is calculated to be \(ca. 3\) from \(Z = (a^2 N_A)/M\), where \(N_A\) is Avogadro’s number \((6.02 \times 10^{23} \text{ mol}^{-1})\) and \(M\) is the molecular weight \((4292.8 \text{ g mol}^{-1})\). The density \((\rho)\) of the complex is about \(2.12 \text{ g cm}^{-3}\), which has been determined by a flotation method.\(^{34,35}\)

The X-ray diffraction pattern of 8-SiW and 10-SiW at different temperatures is presented in Fig. 5(c) and (d). Three different Bragg peaks can be observed in the low angle range. The intensities of peaks 2 and 3 of 8-SiW and 10-SiW are much weaker than the intensity of peak 1, and their intensities decrease with an increase in temperature, disappearing completely at 125 °C and 200 °C, respectively. For 8-SiW, at 100 °C three peaks with a ratio of about \(1 : \sqrt{2}:1/2\) are observed \((d_1 = 18.7 \text{ Å at } 2\theta = 4.77^\circ, d_2 = 11.5 \text{ Å at } 2\theta = 7.70^\circ, d_3 = 9.6 \text{ Å at } 2\theta = 9.20^\circ)\). The X-ray diffraction pattern of 10-SiW at 150 °C presents three peaks with a ratio of about \(1 : \sqrt{2}:1/2\) \((d_1 = 20.2 \text{ Å at } 2\theta = 4.36^\circ, d_2 = 12.5 \text{ Å at } 2\theta = 7.07^\circ, d_3 = 10.6 \text{ Å at } 2\theta = 8.31^\circ)\). Their ratio values indicate that the phases of 8-SiW and 10-SiW are neither cubic nor hexagonal. However, the ratios of \(d_1\) to \(d_2\) are both about 1.6 in 8-SiW and 10-SiW. Consequently, we think that the phases of 8-SiW and 10-SiW are of a pseudo-lamellar structure with layer spacings of 18.7 Å and 20.2 Å, respectively, and the secondary diffraction may be due to the regularity in the position of the polyoxoanions within the layer. This result is similar to a previous study and the slight difference may be due to the change in the synthesis conditions and the central atom of polyoxoanion.

In this series of POM-based ionic complexes, through XRD analysis, we know that when the length of the alkyl chain of the cation increases from short to long, the phase of the aggregate changes from cubic to lamellar as shown in Fig. 6. In the cubic phase the molecules are organized in spheroidal aggregates due to electrostatic interactions. The spheroids have a core–shell structure, where each polyoxoanion is surrounded by quaternary ammonium cations. The cationic alkyl chains are relatively short in 4-SiW and 6-SiW and can be seen as the...
4 Conclusion

In this paper, we successfully synthesized a series of tetra-n-alkylammonium POM ionic complexes by a straightforward ion exchange reaction. These materials have a liquid crystalline property due to the self-organization and nanoscale microsegregation, though there is no mesogenic unit in the complexes. The results of the study show that length of the cationic alkyl chains affects the self-assembly behavior and the thermal properties of the ionic complexes. Shorter alkyl chain complexes tend to form cubic supramolecular aggregates and exhibit high thermal stabilization, whereas longer alkyl chains are found to favor mesophases and tend to form lamellar aggregates. These investigations contribute to the understanding and control of the self-assembly behavior of POM-based ionic complexes, and promote the application of these materials in various functional devices.

Acknowledgements

This work was supported by the NSFC (Grants 21171032 and 21231002), the Fundamental Research Funds for the Central Universities (Grants 09ZDQD0015), and the Open Research Fund of the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (Jilin University, Grant 2012-10).

Notes and references