Cocrystallization of a Poly(ethylene–butene) Random Copolymer with C_{24} in n-Decane

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Received November 26, 2001; Revised Manuscript Received February 4, 2002

ABSTRACT: Amorphous–crystalline random copolymers containing ethylene and butene (PEB) segments are known to self-assemble in solution to yield one-dimensional micellar structures, i.e., rodlike aggregates. This behavior stands in contrast with the amorphous–crystalline diblock polymers, where self-assembly leads to a core consisting of a rough textured plate of polyethylene cloaked by the amorphous component; either alternating poly(ethylene–propylene) or random poly(ethylene–butene). These materials serve as nucleation platforms for wax crystal size control in commercial formulations for middle distillate fuels. Here, we present small-angle neutron-scattering results to evaluate the influence of C_{24} wax in the presence of the PEB random copolymer upon the self-assembly event. In stark contrast to the rodlike micelles the random copolymers cocrystallize with the wax in thin sheets consisting of a single paraffin layer surrounded by amorphous polymer hairs on both plate sides. Such structures have not been seen before. The polymer brush is well-defined, indicating a homogeneous distribution of the polymer in the wax-stabilized plate. It can be conjectured that this behavior may prove to be a viable mechanism regarding the development of flow improvers for waxy crude stocks.

I. Introduction

Recent investigations have shown that wax crystal modifiers based on polyethylene–poly(ethylene–propylene) (PE–PEP) diblock copolymers function as nucleators for wax crystal size control in middle distillate fuels. This diblock copolymer has also shown, on the laboratory scale, the capacity to serve as a flow improver in waxy crude oils. These materials, under proper self-assembly to yield plate structures† that in turn serve as wax crystal nucleation platforms by providing large PE surface areas. They self-assemble to form expansive aggregates consisting of a PE core cloaked behind the amorphous PEP brush layer. The PE plate thus promotes nucleation of solubilized long chain paraffins. The thermodynamics of the diblock copolymer aggregation to hairy platelets has been described in terms of a free energy function based on the structural data obtained from small-angle neutron scattering (SANS). From these results, it may be assumed that other wax crystal modifiers function on the basis of polymer aggregation, where the micelles act as nucleation sites.

This behavior invites the evaluation of other polymer architectures where semicrystalline and amorphous segments are combined in an alternating manner. Candidate structures include copolymers, where the composition variation signals the alteration between semicrystalline and amorphous segments. One such family are nearly random copolymers of ethylene and 1-butene; the PEB-n systems where n is the number of ethyl-groups/100 backbone carbons. These materials, in the bulk, retain a crystalline melting point up to about n = 14. In this manuscript, we report on a series of experiments, where we studied the cocrystallization behavior of PEB-11 together with linear C_{24} in decane solution. In contrast to the PE–PEP diblock PEB-11 self-assembles in open rodlike structures. While for the diblock copolymer the self-assembly occurs around 60 °C, the PEB-11 system shows the first signs of self-assembly only below 0 °C.

After a description of the sample synthesis and characterization, we brieﬂy present some basic features of small-angle neutron scattering emphasizing the contrast variation approach. Thereafter, experimental results under different contrast and different wax-to-polymer ratios are presented for a wide range of temperatures. From these results a picture of wax–copolymer cocrystallization evolves, where at low wax-to-polymer ratios large combined wax–polymer platelets dominate, in which, for wax surplus, these plates appear to serve as nucleation templates for three-dimensional wax crystal growth.

II. Experimental Section

A. Synthesis and Characterization. The PEB materials were made in cyclohexane from either hydrogenous or perdeuterated 1,3-butadiene using standard anionic polymerization techniques. Following synthesis, the samples were then saturated with hydrogen. The palladium on barium sulfate system was used. H NMR (h-polybutadiene) or C NMR
structure factors as a function of wavelength. For a ternary system containing oil, polymer and wax at a position \( r \), the volume fraction of monomer or molecule \( i \) is given by

\[ \phi_i = \frac{V_i}{V} \]

where \( V_i \) is the volume of the molecule \( i \) and \( V \) is the volume of the sample. In this way, eq 3 all but one of the partial structure factors may be made invisible. For the polymer solutions in decane, the maximum contrast is achieved using fully protonated polymers in a fully deuterated solvent.

The small-angle neutron scattering (SANS) data were accumulated at the SANS facilities KWS-1 and KWS-2 at the FRJ-2 research reactor in Jülich, Germany and at NIST in Gaithersburg, Maryland. The Q ranges were 0.0015 < Q < 0.14 Å\(^{-1}\) and the data were corrected for the scattering from the background.

**Table 1. Molecular Characteristics and Scattering Properties of the Chemicals Investigated**

<table>
<thead>
<tr>
<th></th>
<th>h-PEB-11</th>
<th>d,h-PEB-11</th>
<th>h-tetracosane</th>
<th>d-tetracosane</th>
<th>h-decane</th>
<th>d-decane</th>
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<tr>
<td>( M_w (g/mol) )</td>
<td>400</td>
<td>6400</td>
<td>338</td>
<td>388</td>
<td>142</td>
<td>164</td>
</tr>
<tr>
<td>( M_w/M_n )</td>
<td>1.02</td>
<td>1.02</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \rho_0 (g/cm^3) )</td>
<td>0.856</td>
<td>0.92</td>
<td>0.80</td>
<td>0.92</td>
<td>0.73</td>
<td>0.84</td>
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<tr>
<td>( V_o (cm^3/mol) )</td>
<td>17.2</td>
<td>18.49</td>
<td>338</td>
<td>388</td>
<td>142</td>
<td>164</td>
</tr>
<tr>
<td>( \rho (10^{10} cm^{-2}) )</td>
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<td>3.72</td>
<td>-0.39</td>
<td>7.04</td>
<td>-0.49</td>
<td>6.58</td>
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</table>

**Table 2. Microstructure of PEB-11\(^\text{a}\)**

<table>
<thead>
<tr>
<th></th>
<th>triads</th>
<th>diads</th>
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<tbody>
<tr>
<td>( r_12 )</td>
<td>EEE</td>
<td>EB + BE</td>
</tr>
<tr>
<td>( r_21 )</td>
<td>EEB</td>
<td>BB</td>
</tr>
<tr>
<td>( r_31 )</td>
<td>EBB</td>
<td>r_12 r_2</td>
</tr>
<tr>
<td>cluster index</td>
<td>0.62</td>
<td>0.34</td>
</tr>
<tr>
<td>( a )</td>
<td>0.045</td>
<td>10.5</td>
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</table>

\( \text{a: E: ethylene, B: butene. EEE and EEB are percentages of ethylene triads and diads; similarly, EEB denotes ethylene–ethylene–butene triads and so on.} \)

the contrast matching technique which concerns the variation of the degree of hydrogenation or deuteration of the different components of the sample. In this way, in eq 3 all but one partial structure factor may be made invisible. For the polymer solutions in decane, the maximum contrast is achieved using fully protonated polymers in a fully deuterated solvent.

Decreasing the temperature, the self-assembly of polymers and paraffin, or common aggregation processes results in the formation of large objects with a characteristic morphology for each of the investigated systems. The scattering from these objects may often be characterized by power laws

\[ I(Q) \sim Q^{-\alpha} \]

where the exponent \( \alpha \) signifies the spatial arrangements of the polymers and paraffin, respectively.

The objects resulting from the aggregation process may assume different shapes like rods, platelets, and so on. The scattering from a rodlike structure is characterized by an exponent \( \alpha = 3 \) in eq 4. Using the Guinier approximation, the cross section for such aggregates has the form

\[ \frac{d\Sigma}{d\Omega} = \phi_{rod}(1 - \phi_{rod})F_{rod} \rho_p^2 \exp(-Q^2\sigma^2/4)/Q \]

where \( F_{rod} = \pi a^2 \) is the perpendicular area of the rod, \( a \) the rod radius, and \( \rho_p \) the volume fraction of rods. Note, for rods partially swollen with solvent, \( \Delta \rho \) is now the contrast between the polymer plus solvent within the rod relative to the solvent.

The scattering of platelets with constant thickness leads to a \( Q^{-2} \) power law. Here, the Guinier approximation has the following form

\[ \frac{d\Sigma}{d\Omega} = \phi_{plate}(1 - \phi_{plate})\Delta \rho^2 2\pi d_{eff} \exp(-Q^2 d_{eff}^2/12)/Q^2 \]

where \( d_{eff} \) is the plate thickness and \( \phi_{plate} \) the volume fraction of the plates. For \( \Delta \rho \) the same remark holds as before.

Aggregates representing 3-dimensional large objects with sharp interfaces and \( Q \gg 1 \) give rise to Porod scattering.

\[ \frac{d\Sigma}{d\Omega} = \phi_{agg} 2\pi \Delta \rho^2 (S/V) Q^{-4} = P_4 Q^{-4} \]

where \( S \) is the surface and \( V \) the volume of the aggregates. Exponents \( \alpha < 3 \) and \( 3 < \alpha < 4 \) in eq 4 relate to mass or surface fractals respectively, while \( \alpha = 4 \) is characteristic for diffuse interfaces.

**C. SANS Experiments.** For the small-angle scattering experiments, a number of samples under different contrast matching conditions were prepared. In each case the polymer volume fraction was kept at \( \phi_{pol} = 0.01 \), while the volume fraction of wax was varied in three steps from \( \phi_{wax} = 0.005 \), \( \phi_{wax} = 0.01 \) to \( \phi_{wax} = 0.02 \). Polymer contrast was achieved \([\rho_{wax} - \rho_{pol}] \approx 0 \) in eq 3] using h-PEB-11 in decanate with deuterated wax. To achieve wax contrast the denaturant PEB-11 was matched by a mixture of h- and d-decane and C\(_2\) was added. The contrast conditions and sample compositions are displayed in Table 3.

The small-angle neutron scattering (SANS) data were accumulated at the SANS facilities KWS-1 and KWS-2 at the FRJ-2 research reactor in Jülich, Germany and at NIST in Gaithersburg, Maryland. The Q ranges were 0.0015 < Q < 0.14 Å\(^{-1}\). The data were corrected for the scattering from the background.
empty cell and the background obtained from a Cd-run. Calibration to absolute intensities was performed by a water and Lupolen standard, respectively. Temperature control was achieved with a precision of ±1 °C in measuring the temperature with a thermocouple in the sample cell. The phase diagrams of C₂₄ in short hydrocarbons were determined recently by Brecevic and Garside. The dissolution lines for C₂₄ in heptane and dodecane are displayed in Figure 1 as a function of C₂₄ volume fraction.

III. Results

We start by recalling the self-assembly properties of PEB-11 (φₚₒₒ = 0.02) in decane without wax. Figure 2 shows the scattering profile of the PEB-11 at −30 °C, wherein it is seen that the mid- to low-Q data shows a gradient of α = −1.64. This demonstrates the existence of a one-dimensional self-assembled structure (see eqs 4 and 5). Thus, contrary to the platelet structures seen previously for the PE–PEP diblocks, where the experimental gradient was α = −2, at low Q, the α = −1.64 value signifies a rodlike quasi-one-dimensional aggregate. Furthermore, we note in the limiting high Q regime a slope α = −1.64 is found, which is indicative of swollen chains. As has been discussed in ref 6, the aggregates contain large fractions of solvent preserving locally the picture of a polymer solution. Figure 3 depicts the temperature evolution of the self-assembly event in displaying the measured cross section at Q = 5 × 10⁻³ Å⁻¹. At this Q, the intensity is sensitive to the occurrence of self-assembled structures. For temperatures above 0 °C single chain cross sections were observed. At T = 0 °C, the first weak evidence for a beginning aggregation process occurs while at −8 °C a robust signal of self-assembly becomes visible.

A. Observations under Polymer Contrast. Figure 4 presents temperature-dependent SANS pattern from the sample with the lowest wax content (φₓₒₓ = 0.005) where the wax was matched by the solvent (sample 1, Table 3). The difference to Figure 2, where the self-assembly of the polymer alone is displayed, is striking. A small addition of wax alters the polymer self-assembly completely which now features 2-d aggregate structures. This is demonstrated by the low-Q data at lower temperature, where dQ/dQ ~ Q⁻² signifies plate scattering (see eq 6) instead that of rods (Q⁻¹). Thus, the presence of the wax changes the aggregation behavior of PEB-11 from rodlike to platelike structures. These platelike aggregates commence to appear first at −4 °C, while at 22 °C the single chain cross section is primarily visible. The data indicate that the wax is cocrystallizing with the PE segments of the random copolymer. Unlike the PE–PEP diblock, which in effect performs as a 2-d aggregate.
nucleation platform, the PEB-11 random copolymer has its self-assembly altered by the presence of wax.

In the Q regime above $Q = 10^{-2} \text{ Å}^{-1}$, the scattering profile departs from the $Q^{-2}$ asymptote in bending toward lower intensities. Obviously, the finite plate thickness becomes important. An evaluation in terms of the Guinier approximation (eq 5) yields the plate thickness $d_{\text{eff}} = 147 \text{ Å}$ as well as the forward scattering at $Q = 0$ of $4.52 \pm 0.02 \times 10^{-3} \text{ cm}^{-1}$.

The scattering data of Figures 6 and 7, in particular at $T = -22 \degree \text{C}$, exhibit a well-defined minimum around $Q = 0.04 \text{ Å}^{-1}$. From such a scattering profile the form factor of the plate may be evaluated. For an infinite plate with a perpendicular density profile $C_p(z)$ the form factor is given by

$$P(Q) = \left| \int_{-\infty}^{\infty} C_p(z)e^{iQz}dz \right|^2$$

(8)

For a rectangular profile of width $d_{\text{eff}}$ we have

$$P(Q) = \left( \sin \left( \frac{Qd_{\text{eff}}}{2} \right) / \left( Qd_{\text{eff}}/2 \right) \right)^2$$

(9)

When the exponential Guinier term in eq 6 was replaced by eq 9, the scattering profile at $T = -22 \degree \text{C}$ and $\phi_{\text{wax}} = 0.02$ was fitted with this function. Figure 8 compares the obtained fit with the experimental data. The dashed line presents the form factor as given by eq 9. The solid line includes in addition the asymptotic diffuse scattering from the monomer correlations within the chains. A good fit evolves yielding $d_{\text{eff}} = 132 \text{ Å}$, agreeing favorably with that of 149 Å which was based upon the Guinier approximation.

### B. Measurements under Wax Contrast.

To achieve wax contrast following eq 3 polymer and solvent scattering length densities need to be matched. This was

![Figure 5. Small-angle scattering results from a solution of PEB-11 ($\phi_{\text{pol}} = 0.01$) and C$_{24}$ ($\phi_{\text{wax}} = 0.005$) in decane in a Guinier presentation (eq 6) at $T = -22 \degree \text{C}$. The slope leads to a plate thickness of $d_{\text{eff}} = 147 \text{ Å}$. The interception with $Q^2 = 0$ gives the forward scattering of $Qd(2d/dQ) (Q = 0) = (4.52 \pm 0.02) \times 10^{-3} \text{ cm}^{-1}$.](Image)

![Figure 6. Small-angle scattering traces from a solution of PEB-11 ($\phi_{\text{pol}} = 0.01$) and C$_{24}$ ($\phi_{\text{wax}} = 0.01$) in decane (sample 2) under polymer contrast at various temperatures. The solid lines indicate the asymptotic $Q^{-2}$ law.](Image)

![Figure 7. Small-angle scattering data from a solution of PEB-11 ($\phi_{\text{pol}} = 0.01$) and C$_{24}$ ($\phi_{\text{wax}} = 0.02$) in decane (sample 3) under polymer contrast at various temperatures. The solid lines indicate the asymptotic $Q^{-2}$ law.](Image)

![Figure 8. Fit of the small-angle scattering data from a solution of PEB-11 ($\phi_{\text{pol}} = 0.01$) and C$_{24}$ ($\phi_{\text{wax}} = 0.02$) in decane (sample 3) under polymer contrast resulting from a combination of eq 9 and 6. The solid line results from a superposition of the aggregate scattering and the single chain contribution.](Image)

<table>
<thead>
<tr>
<th>$\phi_{\text{wax}}$</th>
<th>$T = -22 \degree \text{C}$</th>
<th>$T = -12 \degree \text{C}$</th>
<th>$T = -4 \degree \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{eff}}$ (Å)</td>
<td>$Qd(2d/dQ) (10^{13} \text{ cm}^{-3})$</td>
<td>$d_{\text{eff}}$ (Å)</td>
<td>$Qd(2d/dQ) (10^{13} \text{ cm}^{-3})$</td>
</tr>
<tr>
<td>0.005</td>
<td>147 ± 0.4</td>
<td>4.52 ± 0.02</td>
<td>121 ± 2.3</td>
</tr>
<tr>
<td>0.01</td>
<td>149 ± 1</td>
<td>4.8 ± 0.03</td>
<td>133 ± 2</td>
</tr>
<tr>
<td>0.02</td>
<td>149 ± 0.4</td>
<td>4.1 ± 0.05</td>
<td>100 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4. Polymer Aggregation Characteristics in the Presence of Wax (Samples 1–3)
always to 2-d structures. Decomposing the observed scattering under polymer contrast from the plate contribution, Porod constant from a 2-d monolayer C24 wax crystals of 32 Å thickness. The polymer plate structures, on the other hand, are about five times as thick and are well described by a homogeneous polymer density distribution across the plates of narrow size distribution. The experimental finding strongly suggests a cocrystallization process, where wax and polymer jointly form platelet structures as is schematically indicated in Figure 12.

Starting from eq 6, we may further evaluate the aggregate structures. Considering the asymptotic forward scattering we have

\[
\frac{d\Sigma}{d\Omega} \bigg|_{\text{wax}} = \phi_{\text{wax}} \Delta \rho_{\text{wax}} \frac{Q^2}{2\pi d_{\text{wax}}} 
\]

and

\[
\frac{d\Sigma}{d\Omega} \bigg|_{\text{pol}} = \phi_{\text{pol}} \Delta \rho_{\text{pol}} \frac{Q^2}{2\pi d_{\text{pol}}} 
\]

Here \(\phi_{\text{wax}}\) and \(\phi_{\text{pol}}\) are the respective volume fractions of the wax and polymer plates in solution, \(\Delta \rho_{\text{wax}}\) is the scattering contrast for wax, \(\Delta \rho_{\text{pol}}\) is that for polymers, and \(\phi_{\text{layer}}\) and \(\phi_{\text{layer}}\) are the wax and polymer concentrations within the layers. In eq 10, they take care of the diluted scattering contrast as a consequence of the polymer or wax admixture, respectively. The
volume fraction of the plates is related to the overall volume fraction of wax or polymer by

\[ \phi_{\text{plate}} = (\phi - \phi_{\text{sol}})/\phi_{\text{layer}} \]  

(11)

Thereby, \( \phi_{\text{sol}} \) stands for the solubilized fraction of the polymer or wax, respectively. Considering the experimentally observed homogeneous polymer distribution (Figure 8) across the layer, we approximately have

\[ \phi_{\text{layer}}^{\text{pol}} = (1 - \phi_{\text{layer}}^{\text{wax}}) \]  

(12)

The plate structures are jointly built from wax and polymer. Therefore, the volume fractions of the wax and polymer plates are related to each other by

\[ \phi_{\text{pol}}^{\text{plate}} = \phi_{\text{wax}}^{\text{plate}} (d_{\text{pol}}/d_{\text{wax}}) \]  

(13)

Using eqs 11–13, we now may rewrite eq 10a and 10b

\[ \frac{d\Sigma}{d\Omega}_{\text{wax}} = \phi_{\text{wax}}^{\text{layer}} \Delta \rho_{\text{wax}} \phi_{\text{wax}}^{\text{layer}} 2\pi d_{\text{wax}} \]  

(14a)

\[ \frac{d\Sigma}{d\Omega}_{\text{pol}} = \phi_{\text{wax}}^{\text{layer}} (d_{\text{pol}}/d_{\text{wax}}) \Delta \rho_{\text{pol}} (1 - \phi_{\text{layer}}^{\text{wax}}) 2\pi d_{\text{pol}} \]  

(14b)

with the measured forward scattering (see Tables 4 and 5), the known contrast factors (see Table 1), and the measured thicknesses; eq 14a and 14b may be used together with eqs 11–13 to calculate the volume fractions of polymer and wax within the platelets as well as total aggregated volume fractions \( \phi_{\text{plate}}^{\text{layer}} \). The results are displayed in Table 6. Finally, the platelet area per cubic centimeter may be evaluated from \( A_{\text{wax}}/V_{\text{plate}} = \phi_{\text{wax}}^{\text{plate}}/d_{\text{wax}} \). The evaluated platelet areas are also given in Table 6.

Figure 13 displays the temperature dependence of the aggregated volume fractions of wax and polymer for \( \phi_{\text{pol}} = 0.01 \) and \( \phi_{\text{wax}} = 0.005 \) ( ), and \( \phi_{\text{pol}} = 0.01 \) and \( \phi_{\text{wax}} = 0.01 \) ( ).

eq 7 then gives \( S/N = 2.57 \times 10^5 \) cm²/cm³. With the assumption of spherical-like crystallites we find an average size of \( a \approx 2400 \) Å. The crystal size obtained in this manner is compatible with the observation of the asymptotic Porod scattering in our range of observation: \( Q_{\text{min}} a = 5 \gg 1 \).

We now address the question, whether the 3-d objects grow independently from the polymer mediated plate structures or whether the polymer/wax plates nucleate the 3-d crystal growth. Qualitatively, the scattering data may be interpreted in both directions. A more quantitative look, however, favors polymer wax platelet as nucleators for the 3-d wax crystals.

1. The polymer structures themselves are always 2-dimensional or at least very close to it (see Figures 4 to 7).

2. Wax and polymer appear to form plates only if \( \phi_{\text{wax}} \leq \phi_{\text{pol}} \).

3. If \( \phi_{\text{wax}} > \phi_{\text{pol}} \), a large number of little crystals with a large surface-to-volume ratio are nucleated, thus already indicating the nucleation function of the primary polymer wax platelets.

4. A close inspection of the polymer scattering traces from the \( \phi_{\text{wax}} = 0.02 \) samples under polymer contrast in Figure 7 shows that the power law indices \( \alpha \) are larger than 2, indicating an admixture of 3-d structures to the polymer scattering. Thus, the polymers to some extent take part in the 3-d structures.

5. If we assume that the polymer would only cocrystallize with the wax into plates and that the rest of the wax crystallizes independently, then, according to Table 6 at \( \phi_{\text{wax}} = 0.02 \), the amount of polymer included in the aggregates would be reduced from \( \phi_{\text{pol}} = 0.0067 \) at \( \phi_{\text{wax}} = 0.01 \) to \( \phi_{\text{pol}} = 0.005 \) at \( \phi_{\text{wax}} = 0.02 \).

6. Finally, the morphology of the wax aggregate changes profoundly in the presence of polymers even if the wax concentration exceeds the polymer concentration by large amounts. 3

These facts together indicate strongly that we are dealing with a staged mechanism where polymer and wax form 2-d platelets which then nucleate 3-d wax crystals. Thus, one may anticipate that these polymers will act as flow improvers for waxy crude oils. 10

V. Conclusions

The experiments on the mixed aggregation of partially crystallizable PEB-11 and wax in decane solution have unraveled a highly interesting cocrystallization process. In the presence of wax, the polymers cocrystallize with the wax in thin sheets consisting of a single paraffin
layer surrounded by amorphous polymer hairs on both plate sides. Such structures have not been seen before. The polymer brush is thus very well-defined indicating a very homogeneous distribution of the polymer in the wax-stabilized plate. The polymer volume fractions in the brush are similar to those in the PE–PEP diblock systems. The conditions for the formation of these aggregates seem to be dictated by a very delicate balance between the enthalpy gain from the cocrystallization and the entropy loss from the conformation entropy of the polymer. The fact that the polymer prefers the cocrystalline state to that of self-aggregation indicates a preferential free energy situation, which could come from a relatively smaller entropy loss due to the paraffin process in the polymer-crystalline aggregates. It is conceivable that at lower temperatures these cocrystallized aggregates may emulate the self-assembled diblock copolymers and act as nucleators for shorter chain paraffin crystals.2

Varying the ethyl branch content of the polymer and possibly the molecular weight could allow a tuning of the aggregation process such that the polymer cocrystallizes with the largest paraffin in a fuel and then subsequently nucleates the lower paraffinic fractions. For such an optimization, systematic studies on the dependence of the aggregation process on PEB crystallinity and paraffin length are required. In particular, the thermodynamics of the process are in need of further understanding. Finally, we wish to note that the presence of the polymer arrests the 3-d growth of the layers. Hence, the act of cocrystallization of PEB-11 with the C24 paraffin creates brush-stabilized single layer paraffin crystals. This behavior may prove to be a viable mechanism regarding the development of flow improvers for waxy crude stocks.

References and Notes

(8) For neutron-scattering experiments at the FRJ -2 in J ü lich see: www.neutronscattering.de.

MA0120456

<table>
<thead>
<tr>
<th>$\phi_{\text{wax}}$</th>
<th>$\phi_{\text{layer}}$</th>
<th>$\phi_{\text{plate}}$</th>
<th>area plate (10$^6$ cm$^2$/cm$^3$)</th>
<th>area $\phi_{\text{wax}}$ (10$^6$ cm$^2$/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = −22 °C</td>
<td>0.005</td>
<td>0.76</td>
<td>0.0028</td>
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<tr>
<td>0.01</td>
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<td>0.81</td>
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*Aggregation parameters from the platelet fraction only.*