Crystallization and Cocrystallization in Supramolecular Comb Copolymer-like Systems: Blends of Poly(4-vinylpyridine) and Pentadecylphenol

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ABSTRACT: The solid state of comb copolymer-like systems obtained by blending poly(4-vinylpyridine) with pentadecylphenol was studied by a combination of techniques. Depending on the amount of pentadecylphenol, several regimes are present. For $0.5 \leq x \leq 1.0$ (x is the ratio between the number of phenol and pyridine groups) the alkyl tails form an interdigitated hexagonally packed crystalline layer. Small-angle X-ray scattering measurements show that for $x = 1.5$ and 2.0 the excess pentadecylphenol cocrystallizes with the associated pentadecylphenol, with the free phenol groups probably aggregating near the middle of the crystalline layer. For $x \geq 2.0$ the orthorhombic crystal modification also appears. Finally for $x \geq 3.0$, part of the excess pentadecylphenol macrophase separates on crystallization, forming an additional phase of pure pentadecylphenol with the familiar orthorhombic packing. These findings are similar to results obtained for *real* comb copolymer systems, i.e., containing covalently bonded side chains. However, our systems are essentially different due to the dynamic hydrogen-bonding equilibrium, which implies that the equilibrium solid state may always involve some form of macrophase separation.

1. Introduction

Nanostructure formation involving supramolecular concepts is a new and exciting branch of science encompassing all kind of systems held together by noncovalent bonds.[1] Recently, these supramolecular concepts have been applied to systems involving polymers and amphiphilic molecules for the design of comb copolymer-like architectures including side chain liquid crystalline polymers.[2–21] Bonding has been achieved using ionic interactions,[5–13] coordination bonding,[14] and hydrogen bonding.[15–21] In recent years, these polymer–amphiphile systems have been studied extensively, and a variety of structures has been realized. In our groups, homopolymers,[17–19] diblock copolymers,[20] and cross-linked polymers[21] have been complexed with flexible nonmesogenic amphiphiles using primarily hydrogen bonding. Depending on a delicate balance between the association interaction and the polar–nonpolar repulsion, an order–disorder transition to well-ordered nanostructures occurs in the homogeneous phase formed by the comb copolymer-like structures. The dynamic amphiphile–polymer complexation equilibrium influences the phase behavior in an essential way. This property, which is absent in conventional comb copolymers, offers unique opportunities to tailor the morphology and phase behavior.[20] In our previous work we considered in detail the phase behavior and nanostructure formation in the molten state.[17–21] Little attention has been paid to the solid state obtained by the crystallization of the alkyl tails of the amphiphiles. To complete the picture, this will be considered in some detail here, and we will demonstrate that the study of the crystallization

behavior provides additional information about the molecular organization.

Our results will be compared with the existing literature on side chain crystallization of *real* comb copolymers, pure and in blends with aliphatic oligomers. Platé and Shibaev[22,23] published the first comprehensive review of the synthesis, structure, and crystalline properties of comb copolymers, discussing in detail the properties of polymers carrying a large number of long hydrocarbon side chains. Several investigations have been devoted to the crystallization,[24–28] usually involving side chain crystallization of comb copolymers with every second main chain atom carrying a side chain. It is well-known that the hydrocarbon side chains preferentially crystallize in the hexagonal crystal structure[23] and that only the outer part takes part in the crystallization; the inner 7–10 CH_2 groups are usually found not to crystallize.[24] The comb copolymer systems investigated form an overall lamellar structure with two possible molecular organizations of the crystalline layers, which can best be described molecularly as interdigitating or end-to-end, respectively.[23,29] Figure 1 illustrates these two possibilities. In the former model the crystalline layer is formed by interdigitating *n*-alkyl side chains pointing in opposite directions; in the latter model the side chains do not interdigitate, and the end groups are next to one another. The factors determining which of the two structures is formed are still a matter of debate.[26,30] As mentioned briefly above, just as diblock copolymers, comb copolymers can microphase separate in the melt in which case the tails of the side chains form separate domains. The effect of the presence of a
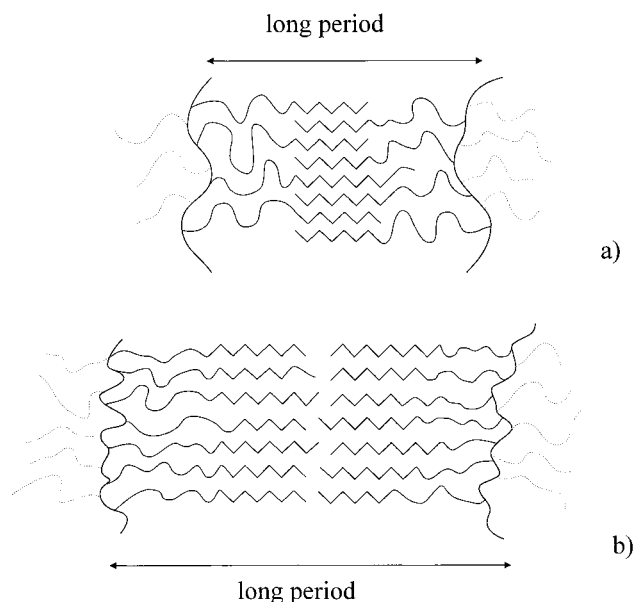
Figure 1. (a) Interdigitating one-layer structure and (b) end-to-end double-layer structure.

microphase separated melt structure on the crystallization and the crystalline structure has been addressed only very recently.[30-32] Ballauf and Schmidt[31,32] reported on the crystallization of the flexible side chains of rigid rod polymers within the layered mesomorphic structure and concluded that the crystallization process proceeded without significant disturbance of the layer structure.

In the case of comb copolymer-like molecules obtained by hydrogen bonding between suitable polymers and amphiphilic molecules, the system is in essence always a mixture of comb copolymer-like molecules and free amphiphiles. For a relative excess of polymer nearly all oligomers will be hydrogen bonded to the polymer, at least at sufficiently low temperatures. However, this is clearly no longer the case for a relative excess of amphiphilic molecules. For *real* comb copolymers a similar situation can be created by considering blends of comb copolymers with "free" side chains. An example from the literature is given by mixtures of polymethacrylates having crystallizable *n*-octadecyl side chains and free "side chains" *n*-octadecanoic acid.[33,34] In these systems cocrystallization was observed between the side chains and the aliphatic oligomers. For small amounts of oligomers, the crystallization behavior in the blend was found to be similar to that of the pure comb copolymer. Larger amounts of aliphatic chains gave rise to more complex phase behavior, not unlike the systems we will consider.

In this article we will focus on the (co)crystallization behavior of blends of poly(4-vinylpyridine) (P4VP) and the amphiphilic molecules pentadecylphenol (PDP). At the temperature of crystallization the hydrogen bonding between P4VP and PDP is nearly complete, and as long as there is no excess of PDP, the system can be considered to consist of comb copolymer-like molecules only. For an excess of PDP the system resembles the comb copolymer blends mentioned above. Both cases will be considered, and the phase behavior will be analyzed using small- and wide-angle X-ray scattering, optical microscopy, infrared spectroscopy, and differential scanning calorimetry.

2. Experimental Section

Materials. 3-Pentadecylphenol (PDP) was purchased from Aldrich and dried in a vacuum oven at 40 °C. Poly(4-vinylpyridine) (P4VP) was purchased from Polyscience Europe GmbH. The molar mass, determined by viscometry in absolute ethanol and DMF using $[\eta] = 2.5 \times 10^{-4} M_w^{0.68}$ and $[\eta] = 1.47 \times 10^{-4} M_w^{0.67}$, respectively, was $M_v = 49\,000$ g/mol.

Preparation of the Complexes. The complexes were prepared from dilute $CHCl_3$ solutions. PDP was dissolved in $CHCl_3$, and subsequently P4VP was added. The mixture was stirred for 5 days at room temperature. Then the $CHCl_3$ was removed by heating the sample. The samples were subsequently dried in a vacuum oven at 40 °C for a week.

Infrared Spectroscopy. The Fourier transform infrared (FT-IR) measurements were performed on a Mattson Galaxy 6021 FTIR spectrophotometer in combination with a MCT detector. The polymer complexes were dissolved in $CHCl_3$ and cast onto a potassium bromide (KBr) window. Before measuring, the samples were cooled to 0 °C to make sure that crystallization had taken place.

Wide- and Small-Angle X-ray Scattering. SAXS/WAXS intensity curves were simultaneously recorded at the beamline 8.2 of the Synchrotron Radiation source in Daresbury, England. For further information about the instrumental setup, see ref 35. Additional experiments were performed on our in-house facilities. For the details of the setup we refer to ref 18.

Differential Scanning Calorimetry. A Perkin-Elmer DSC-7 was used to investigate the samples. The samples were annealed at 200 °C for 5 min and then cooled at 10 °C/min to −70 °C. After 5 min the samples were subsequently heated with a heating rate of 10 °C/min. To investigate recrystallization, a TA-Instruments T-MDSC 2920 (temperature modulated DSC) was used employing an average heating rate of 1 °C/min and a modulation amplitude and period of 0.15 °C and 60 s, respectively.

Optical Microscopy. The P4VP complexes were investigated with a Zeiss Axiophot microscope equipped with a hot stage. The samples were heated for 5 min at 100 °C and subsequently cooled to 10 °C. They were kept at this temperature for several minutes and subsequently heated to 50 °C. Photographs of the samples between crossed polarizers were taken.

3. Results and Discussion

The polymer/amphiphile blend systems will be denoted as P4VP(PDP)$_x$, where x denotes the number of amphiphile molecules per pyridine group. In this investigation x varies from 0.15 to 5.0. For $x > 1.0$, there is an excess of PDP, and the system is essentially a blend of free PDP and P4VP complexed with PDP. The melt state of these systems has been thoroughly investigated.[17,18] Upon cooling, the complex goes, for suitable values of x, from a homogeneous to a microphase separated lamellar state in which the aliphatic tails of the hydrogen-bonded PDP are microphase separated from the rest of the structure. For moderate to full complexation, $0.5 \le x \le 1.5$, the corresponding order−disorder transition (ODT) occurs in the 35−65 °C range. For smaller and larger values of x an ODT is no longer observed. The transition temperatures are presented in Figure 2. Since P4VP is an amorphous polymer, the crystallization, which is the subject of the present paper, is restricted to the PDP molecules. For all compositions studied, $0.15 \le x \le 5.0$, the samples crystallize on cooling.

Crystal Structure. The crystallization of long hydrocarbon chains is very well-known, and various crystal modifications can occur. A hexagonal (α_H), orthorhombic (β_0), triclinic (β_T), or monoclinic (β_M) structure can be formed. The actual structure observed depends on the length of the *n*-parrafins and on the
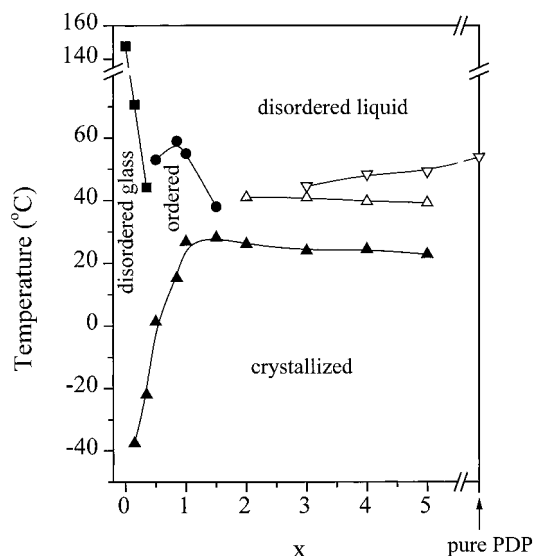
Figure 2. Phase diagram of P4VP(PDP)$_x$: ■, glass transition; ●, order–disorder transition; ▲, T_{m1}; △, T_{m2}; ▽, T_{m3}.
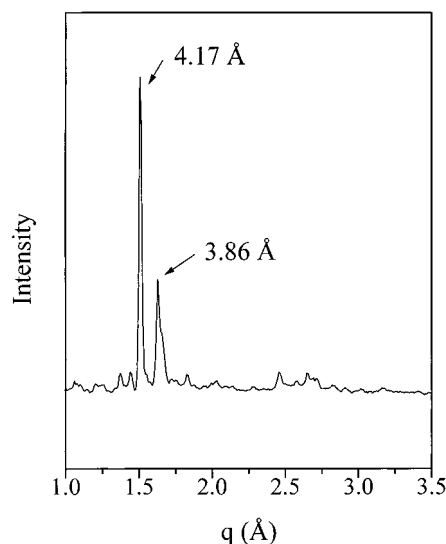

Figure 3. WAXS spectrum of pure PDP. The strong peaks at 4.14 and 3.86 Å indicate an orthorhombic crystal structure.
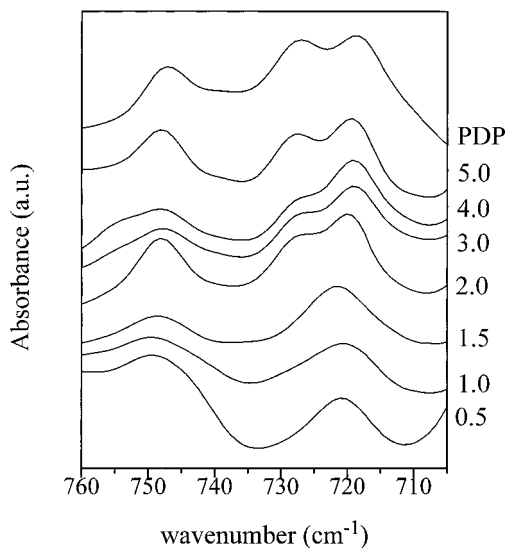

Figure 4. FT-IR spectra for P4VP(PDP)$_x$. A single peak at 721 cm^{-1}, which corresponds to a hexagonal structure, is observed for $x \leq 1.5$. Two peaks at 719 and 727 cm^{-1}, which are observed for $x \geq 2.0$ and pure PDP, indicate the presence of the orthorhombic structure.

number of C atoms being odd or even.[36] End group packing is an important factor influencing the relative stability of the crystal structures, an influence that diminishes for longer chain lengths. Originally, it was believed that the side chains crystallize in the same way as polyethylene, i.e., in an orthorhombic lattice. Later Platé and Shibaev[22] showed that the side chains in comb copolymers crystallize mainly in an α_H packing. The main chain is atactic and tries to maintain a disordered conformation.[37,38] In the α_H phase the chains are arranged perpendicularly to the plane formed by the amorphous main chains.

Long aliphatic hydrocarbons show a characteristic spectrum in wide-angle X-ray scattering (WAXS), and the peaks can be assigned to the different crystal structures.[36,37,39] In the WAXS spectrum of the hexagonal (α_H) structure the main diffraction corresponds to 4.2 Å. For the orthorhombic (β_O) structure there are two main diffractions corresponding to 4.2 and 3.8 Å, and the triclinic (β_T) form has its main diffractions at 4.5, 3.8, and 3.6 Å. The results of WAXS measurements on pure PDP are presented in Figure 3, which demonstrates the occurrence of strong reflections corresponding to 4.17 and 3.86 Å. Hence, the long aliphatic tail of pure PDP crystallizes mainly in the β_O form. Some faint peaks, not belonging to the orthorhombic structure, are present as well, indicating that a small part of the PDP is crystallized in a different structure. In the WAXS data of P4VP(PDP)$_x$ with $x \leq 1.5$, only a single strong reflection at around 4.17 Å can be seen; no sign of a peak corresponding to 3.86 Å is present. Hence, in close analogy with the findings in *real* comb copolymers, the PDP "side chains" crystallize in an α_H structure. For $x \geq 2.0$ two reflections at 4.17 and 3.81 Å appear, indicating the presence of an additional orthorhombic structure.

In FT-IR measurements, the different crystalline modifications of aliphatic compounds are also characterized by specific absorption bands.[40] Crystalline long alkyl chain compounds are characterized by absorption in the 720 cm^{-1} region associated with the CH$_2$ rocking mode. A doublet can be correlated with the orthorhombic packing β_O of the hydrocarbon chains with absorptions at 719 and 727 cm^{-1}, while a single band can be correlated with hexagonal α_H or triclinic β_T packed

chains having one band at 720 or 717 cm^{-1}, respectively. The results of our FT-IR measurements are presented in Figure 4. For pure PDP two bands are visible at 718 and 727 cm^{-1}, confirming the orthorhombic crystal structure. For P4VP(PDP)$_x$, with $x \leq 1.5$, only one band is visible in the 720 cm^{-1} region at 721 cm^{-1}, in agreement with the conclusions from the WAXS measurements that a hexagonal packed crystalline structure is formed. For $x \geq 2.0$ two bands are visible at 719 and 728 cm^{-1}, showing that the orthorhombic crystal structure is present. The intensity of the 728 cm^{-1} peak relative to the 719 cm^{-1} peak for the samples with $x \geq 2.0$ is smaller than for pure PDP, indicating that the α_H and the β_O structure are existing together. This must somehow be due to the presence of "free" PDP. However, for $1.0 \leq x \leq 1.5$, where nonassociated PDP is also present, the system crystallizes exclusively in the α_H form. We will return to these issues further on but first concentrate on the nature of the molecular packing, i.e., interdigitating versus end-to-end, for the stoichiometric case $x = 1.0$.

Table 1. Long Periods of Crystallized Pentadecane, PDP, P4VP(PDP)$_{1.0}$, and P4VP(NDP)$_{1.0}$

sample	d (Å)
pentadecane	21.0
PDP	26.2
P4VP(PDP)$_{1.0}$	36.5
P4VP(NDP)$_{1.0}$	40.9

Nature of Crystalline Layer for $x = 1.0$. Systems of comb copolymers with crystallizable side chains are known to crystallize with either an interdigitating or an end-to-end packing of the crystalline layer (Figure 1).[23,29] Recently, various investigators discussed the conditions that promote the formation of these alternative structures.[26,30] A flexible backbone can adjust very well to close packing of the side chains, resulting in an end-to-end type packing. Enhanced rigidity of the backbone chain as well as the presence of bulky groups causes considerable conformational distortions of the junctions of the backbone and the side chains. The result is an increased volume of the backbone chain and severe hindrance to close packing of the side chains. In this case crystallization is achieved by packing interdigitating side chains into a hexagonal structure.

In the SAXS measurements of crystallized P4VP-(PDP)$_{1.0}$ and P4VP(NDP)$_{1.0}$, where NDP is nonadecylphenol, generally a strong first-order reflection as well as a weak second-order peak has been observed.[17,19] The measured long period d is presented in Table 1 together with the long period of PDP and pentadecane.[36] The n-alkanes pentadecane and nonadecane crystallize in the orthorhombic β_0 crystal structure just as PDP. In the orthorhombic structure as well as in the hexagonal structure the chains stretch perpendicular to the end group planes. Therefore, the long periods measured in these systems correspond to the actual length of the molecules. Because in the α_H structure the chains crystallize perpendicular to the end group planes, the aliphatic tails of the P4VP(PDP)$_{1.0}$ complex are likewise assumed to crystallize more or less perpendicular to the plane formed by the P4VP backbone. When the long period of the complexed P4VP(PDP)$_{1.0}$ (36.5 Å) is compared to the long period in pure PDP (26.2 Å) or with the long period in pentadecane (21.0 Å), we observe that it contains the length of the alkylphenol only once. Furthermore, the difference in long period between P4VP(PDP)$_{1.0}$ and P4VP(NDP)$_{1.0}$ is only 4.4 Å, which is 1.1 Å per CH$_2$ unit. This value, which is slightly smaller than the theoretical value of 1.27 Å/CH$_2$ unit for an all-trans conformation, demonstrates that the packing of the complex must be in the interdigitating form. This is also corroborated by the fact that the SAXS spectra of the P4VP complexes show a second-order peak.[17] Theoretically[41] and experimentally[23] it is well-known that only odd orders are found in the spectra of double-layered materials. Since the end-to-end form is essentially a double-layered structure, all observations indicate that the P4VP(PDP)$_{1.0}$ complexes do have a single-layer structure with *interdigitating* alkyl tails of PDP stretched perpendicular to the main chain, i.e., Figure 1a. This is in good agreement with the observation that a bulky backbone makes ordering of the side chains more difficult, resulting in an interdigitating structure. We will now consider the crystallization behavior for a range of x values in more detail.

Crystallization Behavior. All samples studied ($0.15 \leq x \leq 5.0$) did crystallize. As can be seen from Figure 2, a second melting point T_{m2} appears for $x = 2.0$
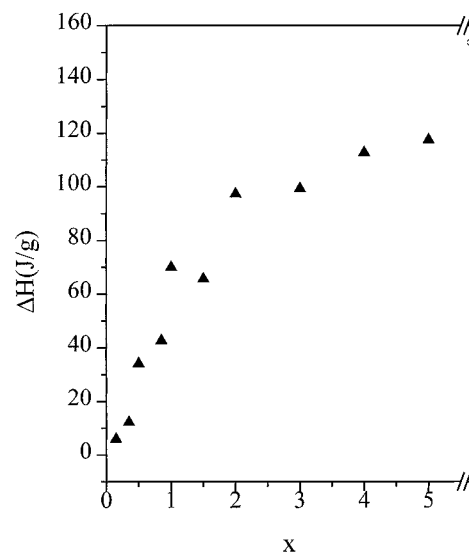
Figure 5. Total melting enthalpy ΔH_m as a function of x.

followed by even a third one, T_{m3}, for $x = 3.0$. The melting temperatures depend on the composition in a manner as presented in Figure 2. The composition dependence of the total melting enthalpy ΔH_m, expressed in J/g of PDP, is presented in Figure 5. ΔH_m increases as a function of x. Furthermore, the melting points T_{m1} and T_{m2} of the associated polymers are lower than for free PDP. Because of the association, the PDP molecules crystallize less perfectly. Jordan et al.[24] found that in comb copolymers the side chains with fewer than 7–10 CH$_2$ groups did not crystallize at all. For side chains with more than 7–10 CH$_2$ groups crystallization took place, but presumably only the outer methylene units participated. We observe an increase in the melting enthalpy (expressed per gram of PDP) with x, signifying that with a more dense packing of the side chains more CH$_2$ groups take part in the crystallization. For *real* comb copolymers, Inomata et al.[33] also noticed an increase in the crystallization enthalpy with side chain density. They reported a large increase for the more rigid main chain polymethacrylates compared to a slight increase for the intrinsically flexible polyacrylates. In contrast with these findings, Yokota et al.[42] and also Magagnini et al.[26] reported that the crystallinity was higher for more widely spaced comb copolymers. Despite the intervening atoms in the main chain, the alkyl side chains of more widely spaced comb copolymers crystallized to a greater extent. The explanation is analogous to what happens in semicrystalline polymer blends where only one of the components is able to crystallize. It is directly related to the glass transition temperature of the amorphous component. A high T_g of the amorphous component prohibits crystallization more at higher concentrations, whereas a low T_g enhances the crystallinity because of the plastification/dilution effect. In our case the amorphous component P4VP has a high T_g, so it is to be expected that the crystallinity increases as a function of x.

The crystallization can be described as to occur in three different regimes, which will now be considered.

First Regime. The first regime consists of the samples with $x < 0.5$, where the P4VP(PDP)$_x$ crystallizes from a homogeneous vitrified system well below the glass transition temperature (Figure 2). As expected and confirmed by the melting enthalpy, only a very small part of the PDP actually crystallizes. The same

phenomenon has been observed in conventional comb copolymers with a glass transition temperature far above the crystallization and melting temperatures T_c and T_m.[43,44] The increase of T_m (and T_c) as a function of x is not really unexpected. The crystallization occurs from a vitrified state, and a higher volume fraction of crystallizable chains increases the probability that larger parts of the alkyl tail can adjust their conformation.

Second Regime. The second regime is formed by 0.5 ≤ x ≤ 1.5, where an order−disorder transition to a lamellar structure takes place on cooling before crystallization sets in.[17,18] At the crystallization temperature the PDP chains are already segregated in microphase separated layers. Since the alkyl tails are already packed together, one might at first sight expect T_m (T_c) and ΔH_m to be independent of x, but surprisingly, all these quantities are still increasing with x. Because P4VP is connected to the PDP, it will lose entropy upon crystallization. This entropy loss is larger for smaller values of x, because more P4VP segments are involved per same amount of PDP molecules. Furthermore, the PDP molecules also have more configurational entropy for smaller values of x (before crystallization they can continuously change their hydrogen-bonding position along the P4VP chains), resulting in a larger entropy loss on crystallization. The melting point will therefore be lower for smaller x. Since ΔH_m is expressed per gram of PDP, a larger value demonstrates that a larger part of the side chains are involved in the crystallization. Apparently, more PDP facilitates the formation of an ordered state of neighboring alkyl tails. Up to $x = 1.5$ this does not result in a different (i.e., orthorhombic) crystal modification because only one melting point is observed for P4VP(PDP)$_{1.5}$, although already a considerable amount of nonassociated PDP is present. Of course, the free PDP is also incorporated in the alkyl layer of the microphase separated melt from which the crystallization proceeds. The free PDP is indistinguishable from the associated PDP, which indicates that it cocrystallizes with the associated PDP. A similar behavior has been reported by Inomata et al.[33,34] for *real* comb copolymers.

Third Regime. The third regime occurs for x ≥ 2.0, where crystallization takes place from a homogeneous melt, i.e., above the order−disorder transition temperature. For x ≥ 2.0 a second melting peak appears around 40 °C, and for x ≥ 3.0 even a third melting peak appears at around 50 °C (see Figure 2). It was shown by DSC and by temperature-modulated DSC measurements that these melting peaks are not due to recrystallization. The assignment of the third melting peak is rather straightforward. Because it is close to the melting point of pure PDP, it must be caused by macrophase separated free PDP. This PDP macrophase separates from the homogeneous melt on crystallization, and the slight lowering of the melting point compared to pure PDP follows from the melting point depression. This is confirmed in separate optical microscopy studies. On crystallization from the homogeneous melt only a single birefringent phase appears for x ≤ 2.0, but two different phases can be distinguished for x ≥ 3.0, which melt at different temperatures (see Figure 6). The total ΔH_m is still increasing with x ≥ 3.0, which is not surprising because the relative amount of free PDP is increasing and the melting enthalpy of free PDP is higher than that of associated PDP.
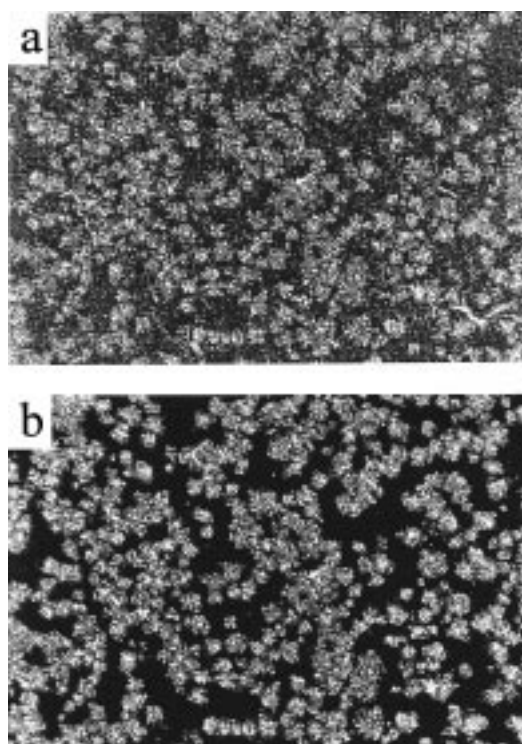

Figure 6. Polarized optical microscopy pictures of P4VP-(PDP)$_{3.0}$. (a) At room temperature, showing two different phases, one with a granular texture and the other with a sperulitic like texture. (b) At 40 °C. The granular texture is melted, and the sperulitic texture is still present.
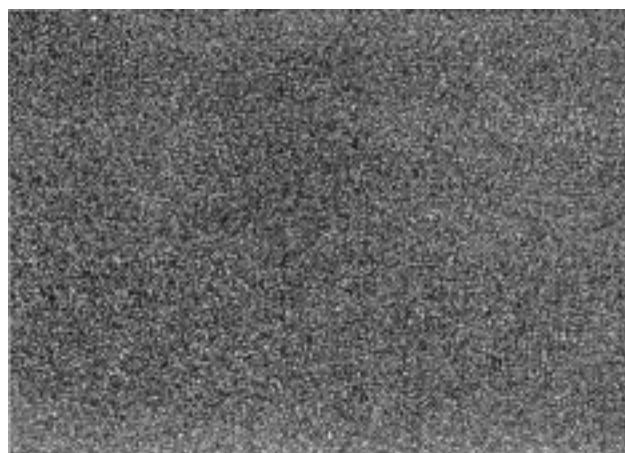

Figure 7. Polarized optical microscopy photograph of P4VP-(PDP)$_{2.0}$ at room temperature.

The appearance of the second melting point T_{m2} for $x = 2.0$ coincides with the appearance of the orthorhombic crystal structure as demonstrated with WAXS and FT-IR. However, in polarizing optical microscopy measurements only one phase with a grainlike structure is observed (Figure 7). On heating, the melting takes place in two stages: first the light intensity of the sample decreases around 25 °C, and finally all crystallinity disappears at 40 °C. We conclude that there is a lamellar phase containing two different kinds of small crystalline domains. The main difference between $x = 1.5$ and $x = 2.0$ is that in the former case the crystallization proceeds from a microphase separated layered structure in which the alkyl chains, including the excess free PDP, are already segregated, whereas in the latter case the crystallization starts from a homogeneous melt state. Whether this is related to the occurrence of an
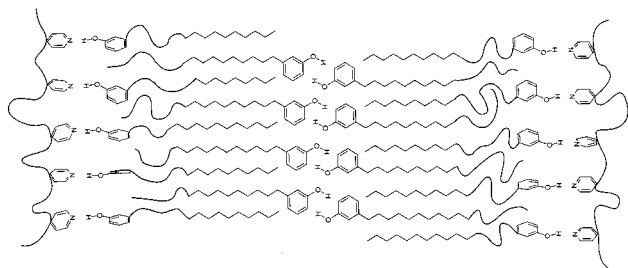
Figure 8. Proposed additional structure for P4VP(PDP)$_x$ with $x > 1.0$.

orthorhombic structure is not known. At any rate, this result shows that for a sufficient amount of PDP the constraints exerted by the P4VP chains diminishes, and the optimal orthorhombic packing starts to occur as well.

Model of the Crystalline Layered Structure. Our next task is to construct a model that explains the above results. We have already argued that for $x \leq 1.0$ crystallization leads to an end-to-end structure as illustrated in Figure 1a. For ≥ 3.0, there is an additional crystalline phase of pure PDP. For $1.0 < x < 2.0$ the excess PDP is somehow incorporated inside the crystalline layers formed by the hydrogen-bonded PDP side chains. The most obvious way is that the free PDP interdigitates with the associated PDP in such a way that the phenol groups are near the middle of the crystalline layer (Figure 8). For values of x close to 1.0 we expect this to be the case in only a small part of the system, the rest being in the end-to-end form. If the free PDP cocrystallizes with the associated PDP and (locally in the case of a small excess of PDP) an interdigitated double layer of PDP is formed, SAXS measurements should reveal a scattering peak at a much smaller angle (approximately halfway) than the main peak for $x = 1.0$. That this is indeed the case can be seen from Figure 9, which represents the SAXS intensity data of P4VP-(PDP)$_{1.5}$ and P4VP(PDP)$_{2.0}$. For $x = 2.0$, the peak at the smallest angle, corresponding to a long period of approximately 70 Å, is already very pronounced. For $x = 1.5$, the same peak is also present but with a much smaller intensity.[17]

In previous publications we reported that the "long period" (based on the sharp peak at $q \cong 1.8$ Å^{-1}) in the P4VP(PDP)$_x$ systems decreased as a function of x.[17] For $x \leq 1.0$ a decrease of the long period with x can be explained in a straightforward manner by the decrease in thickness of the amorphous P4VP-containing polymer layer.[45] A further decrease of the "long period" with x for $x \geq 1$ is now seen to be a consequence of the incorporation of free PDP inside the crystalline layer. Besides the additional peak at much smaller angle, an excess of PDP will also give rise to a scattering peak corresponding to the distance from the middle of the amorphous P4VP-containing layer to the middle of the PDP layer where the phenol groups are segregated. It is quite obvious that this distance is slightly smaller than the long period of the interdigitating Figure 1a structure. Since both structures are present in proportion to the excess of PDP, this model thus explains the observed gradual decrease in $2\pi/q^*$ with x, where q^* is the wavevector corresponding to the main scattering peak. For $x \geq 3.0$, crystallized pure PDP is present, which obviously gives rise to an additional scattering peak corresponding to its long period of 26 Å.
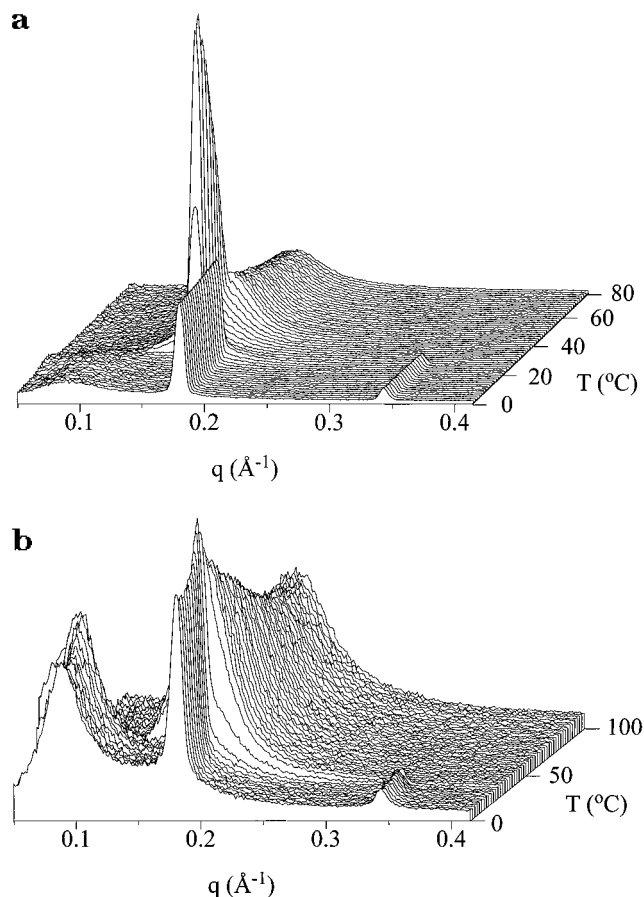

Figure 9. SAXS spectra for (a) P4VP(PDP)$_{1.5}$ and (b) P4VP-(PDP)$_{2.0}$, showing the extra peak at small angle appearing on crystallization.

4. Concluding Remarks

In this paper we considered crystallization in mixtures of P4VP and PDP which, due to hydrogen bonding, lead to comb copolymer-like structures. Denoted as P4VP(PDP)$_x$ we considered various compositions in the range $0.15 \leq x \leq 5.0$. For $x > 1.0$ we are essentially dealing with a blend of comb copolymer-like molecules and free PDP. For $x < 0.5$ and $x > 1.5$, the crystallization starts from a homogeneous state, whereas for $0.5 \leq x \leq 1.5$ it starts from a microphase separated lamellar state. For $0.5 \leq x \leq 1.0$, the crystallization leads to a single crystalline layer structure with interdigitating alkyl tails of PDP, crystallized in a hexagonal structure. For an excess of PDP several situations occur. For x up to 2.0, all "free" PDP is incorporated in the crystalline layers, leading to an interdigitated double layer with the phenol groups of the "free" PDP probably aggregated in the middle. In the SAXS this leads to a development of a characteristic scattering peak at much smaller angle. For $x = 1.5$, the alkyl tails are packed into a hexagonal lattice. For $x = 2.0$, where the crystallization proceeds from the homogeneous melt, an additional orthorhombic packing is present, which melts at a higher temperature. For $x \geq 3.0$, part of the free PDP macrophase separates from the rest of the system on crystallization. In this case the pure PDP crystallizes in the orthorhombic structure with an even higher melting point. The rest of the system contains again both crystal modifications, although the fraction of hexagonally crystallized side chains strongly diminishes with x.

In many respects the behavior of our comb copolymer-like systems is similar to that of real comb copolymers. However, there is also one important difference. For our systems we are dealing with a dynamic hydrogen-bonding equilibrium in a mixture of an amorphous and a crystallizable component. In that case it cannot be excluded that the real *solid-state* equilibrium corresponds to (nearly) all PDP molecules macrophase separated from the P4VP. In fact, we have seen many examples of macrophase separation after prolonged annealing at room temperature. However, for practical applications based on the structure formation of these kinds of supramolecular complexes, such as for instance considered in ref 20, this is not an essential complication since PDP can be simply replaced by similar noncrystallizable amphiphiles.

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