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Asymmetric supramolecular double-comb diblock copolymers: From plasticization, to confined crystallization, to breakout

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ABSTRACT

The combination of asymmetric P4VP-*b*-PAPI diblock copolymers (i.e. $f_{P4VP} \neq f_{PAPI}$) and 3-NDP surfactants in hydrogen-bonded [poly(4-vinylpyridine)-*block*-poly(*N*-acryloylpiperidine)](3-nonadecylphenol)_x (P4PA(3-NDP)_x) supramolecular double-comb diblock copolymers could potentially result in rather interesting morphologies. However, plasticization of the copolymer and the ability of 3-NDP to crystallize were found to affect their self-assembly significantly. In general, for high comb densities x , the complex's tendency to crystallize and its preference to form a flat interface dominated microphase separation. Lower values of x on the other hand gave uneven distribution of 3-NDP, resulting in a higher glass transition temperature of the P4VP block. Crystallization of 3-NDP's aliphatic tails was therefore in most cases restricted to the preferential PAPI microdomains, thereby maintaining the large length scale block copolymer morphology that was already present in the melt. Such behavior is identical to self-assembly of linear semicrystalline diblock copolymers, as in these type of systems structure formation depends on the segregation strength and relative magnitude of the order-disorder transition (T_{ODT}), T_g and T_c , leading to mechanisms like confined crystallization or breakout.

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1. Introduction

A combination of supramolecular chemistry and self-assembling block copolymers enables facile design of complex macromolecular architectures [1]. Such systems often lead to complex phase behavior in bulk [2], solution [3,4] and thin film [5], that in conventional, covalent block copolymers can usually only be achieved by inclusion of three [6–10] or more blocks [11,12]. In addition, the presence of such noncovalent bonds can give rise to dynamic phase behavior, meaning that the structure can be manipulated by external stimuli, like temperature [13].

Most supramolecular block copolymer-based materials originate from a combination of regular, linear (block) copolymers and small surface active molecules, resulting in a comb-shaped copolymer [14]. Association between both components can be via ionic interactions [15–17] or hydrogen bonding [18], whereas sufficiently strong repulsion of the surfactant's tail from a relatively polar polymer backbone forces the complex to self-assemble into a

layered structure. Although many different supramolecular comb-shaped copolymers have been reported in literature, still one of the most employed comb copolymers is based on poly(4-vinylpyridine) (P4VP) and alkylphenol amphiphiles [19]. When combined with polystyrene-containing diblock copolymers, simultaneous phase separation of the PS-*b*-P4VP diblock and the P4VP(alkylphenol) comb block causes spontaneous formation of hierarchical structures, i.e. structures within another structure. Besides lamellae-*in*-lamellae [2], also other structures like cylinders-*in*-lamellae and lamellae-*in*-spheres have been identified by adjusting the composition of PS-*b*-P4VP, while keeping the comb density constant [20].

Double-comb diblock copolymers have recently been realized by replacing the PS block by another block capable of accepting hydrogen bonds, similar to P4VP [21]. Several different internal structures were observed in both copolymer phases of [poly(4-vinylpyridine)-*block*-poly(*N*-acryloylpiperidine)](3-nonadecylphenol)_x (x represents the ratio between 3-NDP amphiphile and monomer) double-comb diblock copolymers by adjusting the side chain density [22] or molecular weight [23]. These studies were, however, limited to symmetric P4VP-*b*-PAPI diblock copolymers, thereby only resulting in lamellar-*in*-lamellar structures

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for relatively high grafting densities ($x = 0.5 - 1.0$).

Since asymmetric diblock copolymers were demonstrated to be readily synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization [24], this work will deal with the combination of several sphere- and cylinder-forming diblocks and comb densities ranging from $x = 0.1$ up to 1.0. Hypothetically rather interesting morphologies, e.g. double lamellae-in-cylinders, could appear in such supramolecular complexes, similar to PS-*b*-P4VP(4-NDP)_{1.0} [20]. As shown in the following, the results obtained are not that straightforward, because additional effects need to be considered to understand the self-assembly of asymmetric double-comb (or bottlebrush) diblock copolymers.

First of all, [P4VP-*b*-PAPI](3-NDP)_x with high grafting densities ($x > 0.3$) contains a crystallizable part (3-NDP) [22], whereas these surfactants plasticize the system above the melting temperature, resulting in a severely reduced glass transition temperature. A crystallizable component is indeed known to affect self-assembly of semicrystalline block copolymers, depending on the relative magnitude of the crystallization temperature (T_c), order-disorder transition temperature (T_{ODT}) and glass transition temperature of the amorphous block (T_g) [25]. Three different regimes should be considered, $T_c > T_{ODT} > T_g$, $T_{ODT} > T_g > T_c$ and $T_{ODT} > T_c > T_g$, generally resulting in two different modes of crystallization. In breakout crystallization, crystallization will overwhelm microphase separation on cooling (i.e., the melt structure is destroyed), whereas in confined crystallization the microphase separation driving force is the stronger of the two, leading to crystallization within the microdomains. Therefore the melt structure is maintained [25].

If $T_c > T_{ODT} > T_g$, crystallization is the first process that will occur, even before an ordered block copolymer structure is formed. Because of the rubbery matrix and the fact that crystallization takes place from a homogeneous melt, the latter will be the dominating mechanism, i.e. breakout. Often a lamellar morphology is observed within a spherulitic superstructure. Examples of such systems include poly(ϵ -caprolactone)-*block*-polybutadiene (PCL-*b*-PB) [26], polyethylene-*block*-poly(ethylene-*alt*-propylene) (PE-*b*-PEP) [27] and polystyrene-*block*-poly(vinylidene fluoride)-*block*-polystyrene (PS-*b*-PVDF-*b*-PS) [28].

When $T_{ODT} > T_g > T_c$, initially a microphase separated structure is formed and on further cooling crystallization will happen within a vitrified matrix. As a consequence, the self-assembled block copolymer structure is maintained, resulting in confined crystallization. Polytetrahydrofuran-*block*-poly(methyl methacrylate) (PTHF-*b*-PMMA) [29] and polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) [30] follow this principle.

The most complex case of the three options is valid for $T_{ODT} > T_c > T_g$, because the mode of crystallization depends on the segregation strength and/or cooling rate. For weakly segregated blocks crystallization still overwrites the ordered microdomains (breakout), such as in poly(ethylene oxide)-*block*-polyisoprene (PEO-*b*-PI) diblock copolymers [31], whereas the ordered morphology is preserved in strongly segregated block copolymer melts. This last type was identified in for instance polyethylene-*block*-poly(3-methyl-1-butene) (PE-*b*-PMB) [32] and polyethylene-*block*-poly(styrene-*r*-ethylene-*r*-butene) (PE-*b*-PSEB) [33].

A second crystallizable block even further complicates the observed phase behavior [34], although crystallization is generally the dominating effect. Phase behavior of such diblock copolymers is often a result of competition between the two crystallizable components and therefore largely depends on the processing conditions, crystallization temperatures, molecular weights and segregation strength [35–37]. In addition, crystallization of the first block may affect crystallization of the second block, also depending on the difference between both T_c s.

Since the side chain density x in [P4VP-*b*-PAPI](3-NDP)_x

(Scheme 1) determines the distribution of 3-NDP and thus whether it is able to crystallize only in a single block or both [22], certain complexes have to be regarded as semicrystalline diblock copolymers. Furthermore, for high grafting densities their macromolecular architecture closely resembles that of conventional, covalent bottlebrush diblock copolymers [38–40]. Because of the semirigid molecular structure, formation of a curved interface is unfavorable. Densely packed bottlebrush copolymers therefore usually have the tendency to form lamellae, even for highly asymmetric compositions [41]. Cylindrical and spherical structures have been characterized for diblocks with sufficient asymmetry in the side chain lengths, though [42,43]. This effect also has to be included for being able to describe and understand the phase behavior of our asymmetric supramolecular double-comb diblock copolymers.

2. Experimental section

2.1. Materials

Three asymmetric P4VP-*b*-PAPI diblock copolymers were synthesized by RAFT polymerization according to the route described in Ref. [24], starting from a P4VP macro-CTA: P4PA131k-22 (131 kg mol⁻¹, $M_w/M_n = 1.34$, $f_{P4VP} = 0.22$), P4PA78k-70 (78.2 kg mol⁻¹, $M_w/M_n = 1.05$, $f_{P4VP} = 0.70$) and P4PA63k-87 (62.9 kg mol⁻¹, $M_w/M_n = 1.14$, $f_{P4VP} = 0.87$). In P4PAy_k-z, y represents the molecular weight in kg mol⁻¹ and z the weight percentage P4VP. 3-NDP was prepared by following the route discussed in Ref. [44]. *N,N*-dimethylformamide (DMF) was of analytical grade.

2.2. Sample preparation

Bulk films of the supramolecular complexes were prepared by casting 2 wt% DMF-based solutions of the diblock copolymer together with the calculated amount of surfactant into glass Petri dishes. Complete evaporation of the solvent in a closed atmosphere was achieved in approximately 5 days (45 °C). Films were thermally annealed at 130 °C for 1 h prior to analysis. Samples of the neat P4PA diblock copolymers were prepared in a similar way, with the only difference being that these were thermally annealed in a vacuum oven at 200 °C for 5 days prior to analysis.

Ultrathin sections (80 nm) for transmission electron microscopy (TEM) were obtained by microtoming in epoxy (Epofix, Electron Microscopy Sciences) embedded pieces of the bulk films using a Leica Ultracut UCT ultramicrotome equipped with a 35 ° DiATOME

Scheme 1. Schematic representation of the [P4VP-*b*-PAPI](3-NDP)_x supramolecular complex. For asymmetric double-combs $m \neq n$.

diamond knife. Enhanced contrast in the complexes was realized by staining the sections with iodine for 10–45 min, whereas the neat P4PA diblocks were stained for at least 2 h.

2.3. Characterization

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q1000 by heating the complexes to 180 °C and cooling to –50 °C at a rate of 10 °C min^{–1}. The second heating cycle was used for analysis.

Small-angle X-ray scattering (SAXS) diffraction patterns were obtained at the Dutch-Belgian Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France [45,46]. The sample-to-detector distance (Dectris Pilatus 1M) of the setup was ca. 4.0 m. The scattering vector q is defined as $q = 4\pi/\lambda \sin \theta$ with 2θ being the scattering angle and λ the wavelength of the X-rays (1.03 Å). For room temperature measurements the acquisition time was 3 min per sample, while for temperature-resolved measurements a 30 s frame time was applied.

Sections of both iodine-stained diblock copolymers and complexes were analyzed on a Philips CM12 electron microscope operating at an accelerating voltage of 120 kV. Images were recorded on a Gatan slow-scan CCD camera.

3. Results and discussion

For studying the self-assembly of asymmetric supramolecular double-comb diblock copolymers, three different P4VP-*b*-PAPI diblock copolymers of varying molecular weight and composition were selected: P4PA131k-22, P4PA78k-70 and P4PA63k-87. Microphase separation of these diblocks resulted in well-ordered P4VP cylinders in a PAPI matrix, PAPI cylinders in a P4VP matrix and PAPI spheres in a P4VP matrix, respectively (Fig. 1). Low scattering intensities, caused by a low electron density difference, only allowed determination of the long periods of the cylinder-forming copolymers (Fig. S1): P4PA131k-22 ($d = 61$ nm) and P4PA78k-70 ($d = 43$ nm).

Double-combs with grafting densities ranging from $x = 0.1$ up to $x = 1.0$ were thoroughly investigated by DSC, TEM and temperature-resolved SAXS. Each P4PA(3-NDP) _{x} complex will be discussed separately with decreasing concentration of 3-NDP and starting with the double-comb with the lowest P4VP content.

3.1. P4PA131k-22(3-NDP) _{x}

In previous studies we observed double perpendicular lamellar-*in*-lamellar morphologies in symmetric supramolecular P4PA(3-NDP)_{1.0} double-comb diblock copolymers, so hypothetically the combination of cylinder-forming P4PA131k-22 and a high concentration of 3-NDP could result in double lamellae-*in*-cylinders, i.e.

small lamellae within both the P4VP cylinders and the PAPI matrix. However, the TEM image displayed in Fig. 2a shows a rather undefined, worm-like structure. Small lamellae can be observed inside the stained P4VP phase. Identical to all other previously investigated $x = 1.0$ complexes, the SAXS profile that was recorded at room temperature (Fig. 3a) only shows ordering at the small length scale, i.e. polymer/amphiphile level ($d_s = 3.9$ nm). As a function of temperature (Fig. S2a) P4PA131k-22(3-NDP)_{1.0} also behaves similar: on melting of the PAPI(3-NDP) comb a large structure appears shortly (highlighted in Fig. 3b) and disappears on melting of the P4VP(3-NDP) comb [47]. An ordered, liquid crystalline lamellar structure lasts in the latter phase up to the order-disorder transition temperature around 70 °C (DSC, Fig. 4).

On cooling from a disordered melt, first the liquid crystalline P4VP(3-NDP) lamellae are formed, simultaneously causing the P4PA block copolymer to microphase separate. Further cooling allows 3-NDP to crystallize within P4VP, whereas the PAPI phase is simply swollen by 3-NDP surfactant. Such a transition gives rise to enhanced scattering of the large length scale, although the limited number of diffraction maxima does not permit a detailed analysis of the type of structure. The $q^*: 3q^*$ ratio could indicate the presence of both lamellae or cylinders with a spacing of 83 nm. Finally,

Fig. 2. TEM images of P4PA131k-22(3-NDP) _{x} supramolecular double-comb diblock copolymers: $x = 1.0$ (a), $x = 0.5$ (b), $x = 0.3$ (c) and $x = 0.1$ (d). Small structures in PAPI (bright phase) could not be resolved due to the applied staining technique (iodine, 10 – 20 min).

Fig. 1. TEM micrographs of neat P4PA diblock copolymers. P4VP appears dark due to staining with iodine. P4PA131k-22 (a), P4PA78k-70 (b) and P4PA63k-87 (c).

Fig. 3. SAXS patterns of P4PA131k-22(3-NDP)_x recorded at room temperature (a) and high temperature (b). *i* denotes the first-order form factor scattering peak of the spherical microdomains.

Fig. 4. DSC thermograms of P4PA131k-22(3-NDP)_x supramolecular double-comb diblock copolymers.

crystallization of the PAPI(3-NDP) comb disrupts the ordered structure completely, ending up with the worm-like morphology as observed by TEM (Fig. 2a). Such a rapid change suggests a breakout-like mechanism, as the inner P4VP(3-NDP) phase may still be rather easily deformed. In addition, this transition affords an energetically more favorable, less curved interface if the melt structure would have been cylindrical.

Lowering the concentration of 3-NDP to $x = 0.5$ still enabled P4PA131k-22(3-NDP)_{0.5} to crystallize (Fig. 4), while the weak diffraction maximum in SAXS only implies short range order at the block copolymer length scale (Fig. 3a, $d = 46$ nm). Interestingly though, a spherical morphology can be clearly observed in TEM (Fig. 2b), meaning that 3-NDP is not equally distributed over both phases. Previously 3-NDP was indeed found to favor PAPI for $x \leq 0.5$ [22]. Even though the broad peak around $q_s = 1.6$ nm⁻¹ suggests the presence of a small structure, no features can be recognized inside the P4VP spheres. Together with the reduced size of the internal structure (4.0 nm vs 4.5 nm for symmetric double-combs) [19], this implies that the majority of 3-NDP is located in the PAPI matrix.

Except disappearance of the small structure, no considerable changes in the large structure can be observed on heating of the complex (Fig. S2b). Stronger scattering does, however, enable a more detailed analysis. At higher temperatures (100–200 °C) additional diffraction maxima appear with a q^* : $\sqrt{8/3}q^*$ ratio (Fig. 3b), typical for face-centered cubic (FCC) spheres [48]. The third, broad peak seen around $q = 0.36$ nm⁻¹ (*i*) originates from the form factor of the spherical microdomains [49], while the absent $\sqrt{4/3}q^*$ maximum may have disappeared in the strong first-order

maximum. Since FCC spheres can usually only be found in a small region of the phase diagram (body-centered cubic, BCC, is the dominant SPH phase) [50], the FCC phase is presumably a metastable phase in this supramolecular complex. As this spherical morphology is preserved on cooling and since all phases are rubbery at room temperature, stronger segregation in P4PA131k-22(3-NDP)_{0.5} apparently leads to confined crystallization of the 3-NDP side chains inside the PAPI matrix, resulting in only mild distortion of the structure.

At lower comb densities (i.e. $x = 0.3$) the complex is still crystalline at room temperature (DSC, Fig. 4) and 3-NDP still favors PAPI, as supported by the presence of a spherical morphology (TEM in Fig. 2c, SAXS in Fig. 3a). Both techniques did not enable detection of a small structure, because the concentration of 3-NDP in the matrix is rather low. Temperature-resolved SAXS profiles illustrated in Fig. S2c show that the shape of self-assembled morphology remains spherical on heating. Only its size was found to increase slightly (37 nm → 40 nm) as a result of the decreased density of the matrix on melting (Fig. 3b). Furthermore, similar to the $x = 0.5$ complex, higher order diffraction maxima became visible at higher temperatures, enabling establishment of the type of packing (FCC). In P4PA131k-22(3-NDP)_{0.3} crystallization of 3-NDP is thus confined in PAPI.

Further dilution of this double-comb to $x = 0.1$ only allowed 3-NDP to plasticize the PAPI matrix. A severely reduced glass transition originating from the PAPI(3-NDP) block can indeed be observed in DSC (Fig. 4, $T_g \approx 35$ °C; for comparison $T_{g,PAPI} \approx 132$ °C). Although the glass transition of P4VP could not be detected (its signal is too weak), based on previous experience (Ref. [22]) we are convinced its position is unaffected in this complex. If 3-NDP is indeed exclusively solubilized in PAPI, the weight fraction $f_{PAPI(3-NDP)} = 0.83$ confirms the formation of P4VP spheres inside a PAPI matrix (Figs. 2d and 3a, $d = 52$ nm). Heating of the sample only led to enhanced scattering and slight expansion of the FCC structure (Fig. 3b and Fig. S2d).

3.2. P4PA78k-70(3-NDP)_x

Addition of stoichiometric quantities 3-NDP to this cylinder-forming block copolymer caused P4PA78k-70(3-NDP)_{1.0} to behave thermally rather similar as compared to the symmetric double-comb discussed in Ref. [22]. It displays two melting points at 46 °C and 55 °C, corresponding to each comb block, and one order-disorder transition at 71 °C in P4VP(3-NDP) (Fig. 5). Identical to all other previously reported stoichiometric double-combs [47], its room temperature SAXS profile only demonstrates an ordered structure at the comb copolymer level (Fig. 6a). TEM on the other

Fig. 5. DSC thermograms of P4PA78k-70(3-NDP)_x supramolecular double-comb diblock copolymers.

Fig. 6. SAXS patterns of P4PA78k-70(3-NDP)_x recorded at room temperature (a) and high temperature (b).

Fig. 7. Electron micrographs of P4PA78k-70(3-NDP)_x supramolecular double-comb diblock copolymers: $x = 1.0$ (a), $x = 0.5$ (b), $x = 0.3$ (c) and $x = 0.1$ (d). The applied staining technique (I₂ vapor, 15–45 min) did not enable imaging of small structures in PAPI (bright phase).

hand proves this complex to self-assemble at the P4PA level as well, although the lamellar-in-lamellar ordering is rather limited (Fig. 7a).

As a function of temperature SAXS does display an ordered large structure at $T_{m,PAPI(3-NDP)} < T < T_{m,P4VP(3-NDP)}$, consistent with a crystalline-amorphous phase (Fig. S3a) as found before [47]. The long period measures 55 nm, whereas the ratio between the first and second order diffraction maximum, i.e. q^* : $2q^*$, could indicate both a cylindrical or lamellar phase (Fig. 6b). If P4VP would be fully occupied by 3-NDP, meaning 3-NDP would be equally distributed, cylinders are expected to be the more stable structure. Crystallization of PAPI(3-NDP) on cooling then explains the appearance of such a worm-like, lamellar structure in TEM, as curvature of the block interface would be minimized. Such a process, i.e. change of structure on crystallization, is a typical example of breakout.

According to DSC P4PA78k-70(3-NDP)_{0.5} is a crystalline material at room temperature. It shows two separate melting points and one T_{ODT} around 80 °C (Fig. 5). All thermal events can be clearly observed in temperature-resolved SAXS (Fig. S3b): upon melting of 3-NDP on the PAPI side a large structure starts to develop at 40 °C, the small structure ($q_s = 1.4$ nm⁻¹) shifts to larger angles

($q_s = 1.5$ nm⁻¹) after having passed the second melting point and finally disappears above the ODT. Scattering intensity of the large structure increases on further heating, but its position remains unchanged ($d = 37$ nm). Higher order reflections were found to be absent, suggesting only short-range order in this complex.

Whereas the diblock copolymer is clearly microphase separated in the melt (Fig. 6b), on cooling to room temperature and in contrast to symmetric double-combs [23], the absence of any scattering peaks at smaller angles implies a disordered block copolymer (Fig. 6a). Since crystallization, and thus the formation of a small length scale, was found to be rather slow in such highly plasticized $x = 0.5$ double-combs, a breakout mechanism can explain this behavior, resulting in the melt structure being overwritten on cooling. The TEM image presented in Fig. 7b supports this interpretation, because only the internal lamellar structure of P4VP ($d_s = 4.5$ nm) can be observed. Apparently P4PA78k-70(3-NDP)_{0.5} is simply too mobile at room temperature in order to maintain its large length scale morphology.

Because 3-NDP showed preference for the PAPI block before, a lower concentration of surfactant caused shifting of the morphology of the neat P4PA block copolymer in P4PA78k-70(3-NDP)_{0.3}. Both SAXS (Fig. 6a) and TEM (Fig. 7c) demonstrated this double-comb to self-assemble into a lamellar morphology with a periodicity of 39 nm. The shape of its thermogram (DSC, Fig. 5) is quite different compared to the symmetric P4PA57k-47 double-comb though [22]: instead of a single, broad melting point, P4PA78k-70(3-NDP)_{0.3} shows one broad melting point (10 °C), an additional melting point at higher temperature (31 °C) and one glass transition (60 °C). Asymmetric distribution of 3-NDP is nicely reflected by this thermal behavior: the first melting point is significantly reduced while the glass transition is somewhat higher in comparison to a P4VP(3-NDP)_{0.3} homopolymer complex ($T_m = 17$ °C, $T_g = 55$ °C). As a result, 3-NDP is much more densely packed in PAPI, giving an increased melting point of the PAPI(3-NDP) comb.

These results in combination with the observation of a higher T_g in P4VP(3-NDP)_{0.1} ($T_g = 90$ °C) allow estimation of the values a and b in P4VP(3-NDP)_a-b-PAPI(3-NDP)_b: $0.1 < a < 0.3$. If $a \approx 0.2$, then $b \approx 0.6$, sufficiently high for formation of a small structure inside PAPI. However, such a feature is not visible in SAXS, but for intermediate values of x comb copolymers were previously demonstrated to give parallel orientation of the internal lamellae [23]. That kind of alignment is only periodic within the PAPI domains, and would therefore never give rise to Bragg diffraction, whereas limitations of our electron microscope did not allow imaging of PAPI's internal structure. Because the structure formation (i.e. 3-NDP crystallization) inside PAPI takes place within a glassy P4VP matrix, the P4PA78k-70(3-NDP)_{0.3} double-comb is a typical example of confined crystallization in semicrystalline diblock copolymers. Finally, as a function of temperature the large structure is unaffected: it remains lamellar up to 200 °C, with almost identical spacing of the long period ($d = 38 \rightarrow 40$ nm, Fig. 6b and Fig. S3c).

For the lowest comb density in P4PA78k-70(3-NDP)_{0.1} 3-NDP only slightly plasticizes the P4VP microdomains ($T_g = 122$ °C; $T_{g,P4VP} = 155$ °C, Fig. 5), similar to symmetric block copolymer-based complexes [22]. As a result, the majority of the amphiphiles is dissolved in PAPI and is thus sufficiently concentrated on this side in order to be able crystallize around room temperature ($T_m = 22$ °C). With such a short PAPI block, b is approximately 0.4 in P4VP- b -PAPI(3-NDP)_b and may therefore form a confined internal parallel lamellar morphology, as was also suggested for P4PA78k-70(3-NDP)_{0.3}. Although this structure cannot be observed in TEM because of the applied staining technique (Fig. 7d), large well-ordered lamellae do appear in this complex due to enhanced mobility of both blocks. Incorporation of 3-NDP almost exclusively

in PAPI confirms such a structure to be most stable, as $f_{\text{PAPI}}(3\text{-NDP}) = 0.47$. On heating of this particular double-comb diblock copolymer, which is actually more closely related to a comb-coil diblock copolymer due to the highly asymmetric distribution of 3-NDP, change of the long period was found to be rather limited ($d = 42 \rightarrow 46$ nm, Fig. 6a and b and Fig. S3d).

3.3. P4PA63k-87(3-NDP)_x

For the lowest molecular weight diblock copolymer, P4PA63k-87, the segregation strength starts to play a crucial role, since $\chi N \approx 19$ [24], meaning that this copolymer is positioned in the weak segregation regime. Addition of 3-NDP decreases this incompatibility even further, because the presence of such surface active molecules usually reduces the interfacial tension considerably [51].

For the $x = 1.0$ double-comb, DSC shows homopolymer-like behavior [44]: besides the ODT of P4VP(3-NDP) around 68 °C, only a single melting point (55 °C) can be detected on heating (Fig. 8). Its room temperature SAXS profile and TEM image (Figs. 9a and 10a, respectively) indeed only display a small lamellar structure ($d_s = 3.9$ nm), caused by polymer/amphiphile self-assembly. These results suggest that the complex is not phase separated on the block copolymer level. Interestingly though, on passing through the melting point (Fig. S4a), according to SAXS the P4PA63k-87(3-NDP)_{1.0} double-comb is still able to form a large length scale structure. The long period measures 42 nm, while one shoulder is insufficient for analysis of the type of structure (Fig. 9b). If the complex is phase separated at both length scales at room temperature, the PAPI phase could be easily confused with the small lamellae formed within P4VP in TEM, since the domain size would only be around 5 nm ($f_{\text{PAPI}} \cdot d = 0.13 \cdot 42$ nm). However, with the available data, nothing can be concluded about its self-assembled morphology.

Similar to P4PA63k-87(3-NDP)_{1.0}, P4PA63k-87(3-NDP)_{0.5} also only displays a single, sharp melting point in DSC (46 °C, Fig. 8). The order-disorder transition of P4VP(3-NDP) increased to 80 °C, identical to the homopolymer-based system P4VP(3-NDP)_{0.5} ($T_m = 49$ °C, $T_{\text{ODT}} = 87$ °C). Reduced chain stretching caused an increase of the size of the internal lamellae ($d_s = 4.4$ nm, Fig. 9a) [19], whereas in contrast to the previous two asymmetric $x = 0.5$ double-combs, scattering was found to be absent at smaller angles. This implies the complex not being phase separated at the block copolymer level. Such behavior is confirmed by the TEM image presented in Fig. 10b: it only shows small lamellae; a distinct PAPI phase cannot be detected. Even in the melt there is no indication of this double-comb being phase separated at the large length scale

Fig. 8. DSC thermograms of P4PA63k-87(3-NDP)_x supramolecular double-comb diblock copolymers.

Fig. 9. SAXS profiles of P4PA63k-87(3-NDP)_x recorded at room temperature (a) and high temperature (b).

Fig. 10. TEM images of P4PA63k-87(3-NDP)_x supramolecular double-comb diblock copolymers: $x = 1.0$ (a), $x = 0.5$ (b), $x = 0.3$ (c) and $x = 0.1$ (d). Stained P4VP domains appear dark (I_2 vapor, 10 min).

(Fig. 9b). Only a slight contraction of the small lamellae is visible on melting ($d_s = 4.2$ nm), that finally vanishes completely when heated above the ODT. Although a very faint shoulder appears briefly in SAXS around T_m (Fig. S4b), such a weak signal is unlikely to be caused by a highly ordered block copolymer structure. The PAPI block is simply too short for being able to give sufficiently strong segregation.

At lower grafting densities, P4PA63k-87(3-NDP)_{0.3}, only very broad peaks can be observed in DSC (Fig. 8) and SAXS (Fig. 9a), almost the same as a P4VP(3-NDP)_{0.3} supramolecular comb-shaped copolymer ($T_m = 16$ °C, $T_g = 57$ °C). The only difference between these two is the presence of an additional, but relatively sharp melting point around 29 °C (other $T_m = 11$ °C, $T_g = 58$ °C). Such a transition indicates the presence of a significant amount 3-NDP inside the PAPI block. However, confirming the SAXS data, only a fiber-like structure could be identified in this complex by TEM (Fig. 10c). On heating of the system (Fig. S4c) a correlation hole peak [52] became visible around $q = 0.26 \text{ nm}^{-1}$ at higher temperatures (Fig. 9b), once again demonstrating this double-comb lacking long-range order. Even though quite some 3-NDP is present in the PAPI phase, this block is simply too small for being able to accommodate a majority of the surfactant molecules, leading to an insufficiently

strongly segregated melt.

In P4PA63k-87(3-NDP)_{0.1} the P4VP block is severely plasticized, as its glass transition is reduced to 103 °C ($T_{g,P4VP} = 155$ °C), although this value is slightly higher compared to P4VP(3-NDP)_{0.1} ($T_g = 91$ °C), which implies uneven distribution of 3-NDP. Because of the high asymmetry of P4PA63k-87, crystallization inside PAPI around room temperature ($T_m = 22$ °C, Fig. 8) is already possible for a modest preference for this block. As opposed to the other three P4PA63k-87(3-NDP)_x double-comb diblock copolymers, the $x = 0.1$ complex does show an ordered, large structure at room temperature (Fig. 9a). The relative positions of the two scattering maxima (i.e. q^* : $2q^*$) could originate from both a lamellar or cylindrical morphology, although the TEM image illustrated in Fig. 10d clearly shows highly asymmetric lamellae (SAXS: $d = 27$ nm). Limited long-range order accounts for the absence of higher order reflections, while the structure remains unchanged on heating (Fig. 9b and Fig. S4d). Estimation of the distribution of 3-NDP was done using the formerly introduced notation P4VP(3-NDP)_a-b-PAPI(3-NDP)_b: assuming that all 3-NDP would be exclusively dissolved in the PAPI microdomains (i.e. $a = 0$), b was calculated to be 1.0. However, such an assumption is undoubtedly incorrect, providing both the plasticization of P4VP and reduced T_m of PAPI(3-NDP) (T_m of PAPI(3-NDP)_{1.0} = 46 °C) [22]. A value for b in the range of 0.3–0.5 would be more realistic, since all symmetric $x = 0.5$ double-comb diblock copolymers were previously found to melt at approximately 35 °C [23].

Interestingly though and regardless of the composition, $f_{PAPI(3-NDP)} < 0.34$ would suggest formation of a cylindrical or even spherical structure, because the phase diagram for PS-*b*-P4VP(3-PDP) coil-comb diblock copolymers was found to be identical to linear AB diblocks [53]. Hierarchical lamellae-*in*-lamellae were discovered for $f_{comb} = 0.35$ –0.63. This system is, however, considerably less complicated than P4PA63k-87(3-NDP)_{0.1}: 3-PDP crystallizes around room temperature, above 100 °C a substantial amount of pyridine is non-hydrogen-bonded, and thus most 3-PDP simply acts as selective solvent around the glass transition of PS. Since hydrogen bonding in acrylamides is stronger than in vinylpyridines [21] and a large quantity of surfactant is present at both sides of the interface, upon vitrification of the P4VP block the structure will be locked in a more preferential, less curved lamellar morphology. Further cooling will lead to confined crystallization within the highly asymmetric PAPI lamellae, possibly enabling the formation of a parallel internal structure that cannot or could not be observed with SAXS and TEM, respectively.

4. Conclusions

Because of the semirigid architecture and their ability to crystallize, asymmetric supramolecular P4PA(3-NDP)_x double-comb diblock copolymers were found to behave rather differently than initially expected. Unlike hierarchical structure formation in the previously reported symmetric double-combs, in high comb density complexes ($x = 0.5$ –1.0) crystallization of 3-NDP generally disrupted the ordered structures that were present in the melt by following a breakout-like mechanism, regardless of the P4PA copolymer composition. This observation was also partially attributed to the complexes' desire to form a flat interface, analogue to all-covalent bottlebrush diblock copolymers. Lowering the surfactant concentration to $x = 0.1$ –0.3 often resulted in asymmetric distribution of 3-NDP, thereby inducing dissimilar plasticization of each block. For most of these double-comb series a small structure was formed within the preferential PAPI block via confined crystallization, although limitations of our instrumentation did not allow direct observation by TEM. A full overview of the self-assembly of the asymmetric double-comb diblock copolymers is

Fig. 11. Overview of the self-assembly of asymmetric P4PA(3-NDP)_x double-comb diblock copolymers. SPH (spheres), LAM (lamellae) and DIS (disordered).

provided in Fig. 11 and Table S1.

All modes of crystallization typical for self-assembling semi-crystalline diblock copolymers were identified in P4PA78k-70(3-NDP)_x, i.e. breakout ($x = 0.5$ and 1.0) and confined crystallization ($x = 0.1$ and 0.3), whereas strong segregation in P4PA131k-22(3-NDP)_x even enabled confined crystallization in a rubbery matrix ($x = 0.3$ and 0.5). For the last diblock copolymer that was analyzed (P4PA63k-87) the segregation strength χN was found to start to play an important role. Since 3-NDP can act as a compatibilizing agent as well, most complexes ($x = 0.3$ –1.0) were observed to be disordered at the block copolymer level, thereby simply behaving like homopolymer P4VP(3-NDP) complexes. By increasing the block copolymer molecular weight, hierarchical structures could hypothetically be found in sphere-forming P4PA-based double-combs, although highly ordered structures cannot be guaranteed, since breakout crystallization can still dominate the phase behavior for high values of x .

A better solution for obtaining ordered hierarchical morphologies in asymmetric supramolecular double-comb diblock copolymers might be the insertion of a glassy, non-hydrogen bond accepting third block. By doing so, vitrification of the middle block in such asymmetric comb-coil-comb triblock terpolymers could lock the melt structure, before crystallization and self-assembly of the internal structure could take place. A similar approach was successfully applied before in PS-*b*-P4VP(4-NDP) coil-comb diblock copolymers, leading to structures like lamellae-*in*-spheres and lamellae-*in*-cylinders.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2017.05.057>.

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