

Self-Assembled Structures in Diblock Copolymers with Hydrogen-Bonded Amphiphilic Plasticizing Compounds

Sami Valkama,[†] Teemu Ruotsalainen,[†] Antti Nykänen,[†] Ari Laiho,[†] Harri Kosonen,[†] Gerrit ten Brinke,[‡] Olli Ikkala,^{*,†} and Janne Ruokolainen^{*,†}

Optics and Molecular Materials, Department of Engineering Physics and Mathematics and Center for New Materials, Helsinki University of Technology, P.O. Box 2200, FI-02015 HUT, Espoo, Finland, and Laboratory of Polymer Chemistry, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT: Hydrogen-bonding amphiphilic low molecular weight plasticizing compounds to one block of diblock copolymers to form supramolecular comblike blocks leads to hierarchical self-assembly at the block copolymer (long) and amphiphile (short) length scales, in which lamellar-in-lamellar order and the related phase transitions have previously been shown to allow thermal switching of electrical and optical properties [*Science* **1998**, 280, 557; *Nat. Mater.* **2004**, 3, 872]. In this work other hierarchies and phase transitions are systematically searched, a particular interest being hierarchies containing gyroid structures and the related order–order transitions. Polymeric supramolecular comb–coil diblock copolymers consisting of a polystyrene (PS) coillike block and a supramolecular comblike block based on poly(4-vinylpyridine) (P4VP) are used, where the pyridines are either directly hydrogen bonded with 3-pentadecylphenol (PDP), i.e., PS-*block*-P4VP(PDP)_{1.0}, or first protonated with methanesulfonic acid (MSA) and then hydrogen bonded to PDP, i.e., PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0}. In this way the comblike block can be noncharged or charged. The morphologies were determined using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) at different temperatures. In the case of PS-*block*-P4VP(PDP)_{1.0}, all classical diblock copolymer morphologies were observed at room temperature, where the P4VP(PDP)_{1.0} domains contain an additional lamellar structure due to the supramolecular comblike blocks. Here we report novel gyroid and hexagonal perforated layer morphologies, i.e., where the PS and P4VP(PDP)_{1.0} blocks form gyroid or hexagonal perforated layer order and the P4VP(PDP)_{1.0} domains have an internal lamellar order. Heating past ca. $T = 60$ °C causes an order–disorder transition within the P4VP(PDP)_{1.0} domains. Further heating leads to gradually reduced hydrogen bonding strength, and importantly PDP becomes soluble in PS at $T > \text{ca. } 120$ °C. At such temperatures PDP is found in both the P4VP and PS domains, thus leading to changes in the relative volume fractions of the domains, which in turn leads to order–order transitions. In PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0}, typically lamellar and cylindrical block copolymeric structures were observed, where there was an additional internal lamellar order within the P4VP(MSA)_{1.0}(PDP)_{1.0} domains. Coincidentally, an order–disorder transition within the P4VP(MSA)_{1.0}(PDP)_{1.0} domains takes place at $T = \text{ca. } 125$ °C. Above that temperature, PDP is in both PS and P4VP(MSA)_{1.0} domains, but most interestingly at ca. $T > 175$ °C PDP becomes a nonsolvent for P4VP(MSA)_{1.0} and it is therefore expelled to predominantly to the PS domains. This manifests as an order–order transition. All samples exhibit at least two thermoreversible order–order transitions, and some of them show even five consecutive self-assembled phases as a function of temperature. Besides being amphiphilic, PDP can also be regarded as a plasticizer, i.e., relatively nonvolatile solvent, for the P4VP, PS, and P4VP(MSA)_{1.0} with characteristic phase behaviors. This, in combination with the comb–coil diblock copolymer composition and the reversibility of the hydrogen bonding, enables to achieve thermoreversible transition sequences that are not easily accessible only by changing the Flory–Huggins interaction parameter χ by temperature, for example transitions from a lamellar to spherical structure. The combination of phase behaviors of self-assembly and polymer/plasticizer mixtures allows new structural hierarchies and phase transitions that may lead to new types of responsive materials.

Introduction

Self-assembly and nanoscale structures in block copolymer and related supramolecular systems have extensively been pursued in an effort to tune the materials properties and functions for stimuli responsive, smart, and functional materials.^{1–12} Responsive polymers have typically been achieved in water solutions using e.g. poly(*N*-isopropylacrylamide) or elastin-like polypeptides, where a detailed control of the chain conformations has been achieved using e.g. temperature, pH, and light.^{13–15} In these systems, the response specifically requires tuning of the hydrophobic and hydrophilic interactions and takes

place only in a “dilute” aqueous environment, where small changes in solvent properties or concentrations may suppress or prevent the response. By contrast, in the solid state, combinations of other types of interactions are required, and in this respect self-assembly and their phase transitions could be useful, such as the order–disorder (ODT) or order–order (OOT) transitions. In block copolymer systems, thermoreversible OOTs between different phases can be thermally induced by varying the Flory–Huggins interaction parameter χ . OOTs have been demonstrated e.g. between body-centered-cubically assembled spheres and hexagonally assembled cylinders,^{16–20} the gyroid phase and hexagonally assembled cylinders,^{21–25} the gyroid and hexagonally perforated layer (HPL) phases,^{21,23,24} the lamellar phase and hexagonally assembled cylinders,^{22,25,26} and the lamellar phase and HPL phase.^{27–29} In addition, irreversible

[†] Helsinki University of Technology.

[‡] University of Groningen.

* Corresponding authors. E-mail: olli.ikkala@tkk.fi; Janne.Ruokolainen@tkk.fi.

Table 1. Characteristic Features of the Diblock Copolymers and the Observed Morphologies of PS-*block*-P4VP(PDP)_{1,0} at Three Temperatures^a

sample code	PS- <i>block</i> -P4VP(PDP) _{1,0}		morphology ^b at			PS- <i>block</i> -P4VP		
	$f_{\text{comb},1}$	total M_w including PDP (g/mol)	25 °C	170 °C	200 °C	$M_{w,PS}$ (g/mol)	$M_{w,P4VP}$ (g/mol)	M_w/M_n
S03.248k.P	0.03	247 800	DIS	DIS		240 000	2 000	1.07
S20.377k.P	0.20	377 400	lam-in-SPH'	SPH'		301 000	19 600	1.19
S24.480k.P	0.24	479 900	lam-in-SPH'	SPH'		365 300	29 400	1.23
S25.45k.P	0.25	45 300	lam-in-CYL'	SPH'		34 000	2 900	1.07
S28.50k.P	0.28	49 500	lam-in-HPL'	SPH'		35 500	3 600	1.06
S35.62k.P	0.35	61 800	lam-in-LAM	HPL'	HPL'	40 000	5 600	1.09
S43.74k.P	0.43	73 700	lam-in-LAM	HPL'	HPL'	42 100	8 100	1.08
S49.64k.P	0.49	64 100	lam-in-LAM	LAM	HPL'	32 900	8 100	1.06
S50.259k.P	0.50	259 000	lam-in-LAM	SPH'		128 400	33 500	1.17
S60.197k.P	0.60	197 000	lam-in-LAM	SPH'		78 900	30 300	1.22
S62.83k.P	0.62	83 300	GYR -in-lam	LAM	HPL'	31 900	13 200	1.08
S63.154k.P	0.63	153 600	lam-in-LAM	LAM	CYL'	57 300	24 700	1.14
S63.129k.P	0.63	129 000	lam-in-LAM	LAM		47 600	20 900	1.14
S71.454k.P	0.71	454 100	CYL ¹ -in-lam	SPH		130 300	83 100	1.35
S75.226k.P	0.75	225 800	CYL-in-lam	LAM		56 300	43 500	1.20
S79.102k.P	0.79	102 100	CYL-in-lam	CYL	LAM	21 400	20 700	1.13
S85.135k.P	0.85	134 500	SPH-in-lam	CYL ¹	HPL	19 900	29 400	1.15
S92.236k.P	0.92	236 100	SPH-in-lam	CYL ¹		18 600	55 800	1.26

^a For the denotions of the morphologies, see Scheme 2. $f_{\text{comb},1}$ denotes the weight fraction of P4VP(PDP)_{1,0}. ^b The prime symbol (') refers to structures where PS forms the matrix; ¹wormlike domains with poor long-range order.

order–order transitions from quasi-stable to stable morphologies have been reported.³⁰

Besides varying the χ parameter, OOTs can also be achieved utilizing supramolecular comb–coil diblock copolymers, as has been demonstrated previously.^{26,31} Comb–coil diblock copolymers consist of a coil block and a comb block, where side chains are regularly grafted to a usually flexible backbone. Such systems can lead to self-assembly at two different length scales: The larger length scale corresponds to the lengths of the different blocks in polymer backbones, and the shorter length scale is determined by the length of the repulsive side chains within the comb block. In supramolecular comb–coil diblock copolymers, the side chains (typically low molecular weight amphiphilic compounds) are attached by physical bonds, such as hydrogen bonding, ionic interactions, or coordination, rather than being covalently linked.³² Therefore, they can also be regarded as specific diblock copolymer/plasticizer systems, where the plasticizer is a relatively high boiling point solvent. Compared to the conventional comb–coil diblock copolymers, the physical bonding of the side chains leads to more rich phase behavior due to the thermal reversibility of the bonding, which may manifest as order–order transitions.^{26,33} Typically these supramolecular complexes also form structure-in-structure self-assemblies.^{26,34–37}

Here we want to address the phase behavior of two PS-*block*-P4VP systems, i.e., PS-*block*-P4VP(PDP)_{1,0}, where 3-pentadecylphenol (PDP) is hydrogen bonded to the pyridines, and PS-*block*-P4VP(MSA)_{1,0}(PDP)_{1,0}, where the pyridines are first protonated with methanesulfonic acid (MSA) and where PDP is then hydrogen bonded to sulfonates. The relative molecular weights of the blocks of PS-*block*-P4VP were selected to cover the entire morphology diagram. Near room temperature the repulsive pentadecyl tails of PDP form a comb-shaped architecture with the P4VP and P4VP(MSA)_{1,0} backbones due to the hydrogen bonding, which leads to self-assembly at a few nanometers length scale and related phase transitions. Therefore, PS-*block*-P4VP(PDP)_{1,0} and PS-*block*-P4VP(MSA)_{1,0}(PDP)_{1,0} can be denoted as supramolecules. On the other hand, PDP can be regarded as a plasticizer, i.e., a solvent which remains as an integral part of the mixture. Therefore, it is instructive to consider the system also in the perspective of polymer/solvent systems for P4VP, PS, and P4VP(MSA)_{1,0} in combination with

PDP and related miscibility and immiscibility behavior for the block copolymeric blocks. Finally, the block copolymer has a tendency for self-assembly at tens of nanometers length scale. The interplay of these mechanisms allows complex phase behavior and hierarchies, to be discussed shortly.

Experimental Methods

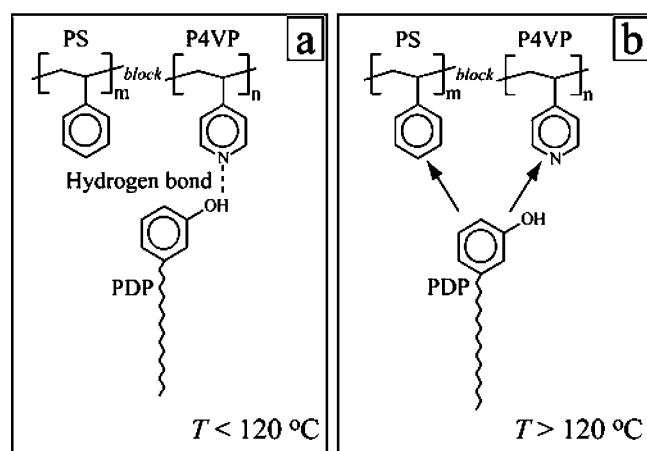
Polystyrene-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP) diblock copolymers were supplied by Polymer Source Inc. and were used without further purification. (For the materials, chemical formulas, and compositions, see Tables 1 and 2 and Schemes 1–3.) Methanesulfonic acid (MSA) was of purity 99%, and it was purchased from Fluka. 3-Pentadecylphenol (PDP) was acquired from Aldrich (purity 98 wt %), and it was purified by recrystallizing twice from petrol ether. PS-*block*-P4VP, MSA, and PDP were dissolved in chloroform separately. The solutions were combined, leading to homogeneous clear mixtures according to the nominal compositions of PS-*block*-P4VP(PDP)_{1,0} and PS-*block*-P4VP-(MSA)_{1,0}(PDP)_{1,0} where there is one PDP and MSA molecule vs one repeat unit of 4-vinylpyridine. The solutions were stirred for 24 h, and the solvent was slowly evaporated at room temperature. Thereafter, the samples were dried in a vacuum at 30 °C and annealed several days at 130 °C under a N₂ atmosphere with 2 bar overpressure and finally slowly cooled to room temperature. Note that the block copolymer compositions are given here by the weight fractions instead of the volume fractions. However, the densities of the PS and P4VP(PDP)_{1,0} phases are close to each other (1.047 and 0.98 g/cm³, respectively), leading to only a rather small difference.³⁴

The X-ray measurements were performed at the Dutch-Belgian beamline (BM26) of European Synchrotron Radiation Facility in Grenoble using a beam of 10 keV with an area of 0.35 × 0.5 mm² at the sample position. The data were collected with a two-dimensional wire chamber camera at a distance of 6–8 m from the sample, corresponding to the q range from ca. 0.005 to 0.08 Å^{−1}. (For a more detailed description of the beamline, see ref 38.) Additional measurements were performed with a SAXS device consisting of a Bruker MICROSTAR microfocussing rotating anode X-ray source with Montel Optics (Cu K α radiation λ = 1.54 Å), where the beam was further collimated using four sets of four-blade slits. The sample-to-detector distances of 1.5 and 0.45 m were used spanning a q range from 0.006 to 0.14 Å^{−1} and from 0.02 to 0.80 Å^{−1}, respectively. Scattering intensities were measured using a 2-D area detector (Bruker AXS). The magnitude of the scattering vector is given by $q = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering

Table 2. Characteristic Features of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} at Different Temperatures^a

sample code	PS- <i>block</i> -P4VP(MSA) _{1.0} (PDP) _{1.0}		morphology ^b at			PS- <i>block</i> -P4VP		
	<i>f</i> _{comb,2}	total <i>M</i> _w including MSA and PDP (g/mol)	25 °C	170 °C	210 °C	<i>M</i> _{w,PS} (g/mol)	<i>M</i> _{w,P4VP} (g/mol)	<i>M</i> _w / <i>M</i> _n
S29.48k.MP	0.29	48 000	lam-in-CYL ¹	SPH'	SPH'	34 000	2 900	1.07
S33.53k.MP	0.33	52 800	lam-in-CYL'	CYL'	SPH'	35 500	3 600	1.06
S35.297k.MP	0.35	297 000	lam-in-SPH'	SPH'	SPH'	193 700	21 400	1.13
S40.67k.MP	0.40	67 000	lam-in-LAM	CYL'	SPH'	40 000	5 600	1.09
S48.81k.MP	0.48	81 100	lam-in-LAM	HPL'	SPH'	42 100	8 100	1.08
S54.71k.MP	0.54	71 400	lam-in-LAM	CYL'	SPH'	32 900	8 100	1.06
S56.44k.MP	0.56	44 100	lam-in-LAM	CYL'	SPH'	19 600	5 100	1.08
S65.225k.MP	0.65	224 700	lam-in-LAM	SPH'	SPH'	78 900	30 300	1.22
S67.95k.MP	0.67	95 400	lam-in-LAM	CYL'	SPH'	31 900	13 200	1.08
S67.217k.MP	0.67	217 200	lam-in-LAM	CYL'	SPH'	71 900	30 200	1.13
S67.176k.MP	0.67	176 100	lam-in-LAM	CYL'	SPH'	57 300	24 700	1.14
S68.148k.MP	0.68	148 200	CYL ¹ -in-lam	CYL'	SPH'	47 600	20 900	1.14
S82.121k.MP	0.82	121 000	CYL ¹ -in-lam	LAM	SPH'	21 400	20 700	1.13
S88.161k.MP	0.88	161 300	CYL ¹ -in-lam	LAM	SPH'	19 900	29 400	1.15

^a For the denotations of the morphologies, see Scheme 2. ^b The prime symbol (') refers to structures where PS forms the matrix. ¹, wormlike domains with poor long-range order.

Scheme 1. Schematics of the PDP Interactions in PS-*block*-P4VP(PDP)_{1.0}^a

^a (a) At room temperature PDP is hydrogen bonded to P4VP and is not soluble (miscible) in PS. Upon heating the hydrogen bonds are gradually broken. (b) At ca. $T > 120\text{ }^{\circ}\text{C}$ PDP becomes soluble also in PS; i.e., PDP is in both P4VP and PS domains.

angle. The heating ($5\text{ }^{\circ}\text{C}/\text{min}$) and cooling rates ($10\text{ }^{\circ}\text{C}/\text{min}$) during SAXS measurements were relatively fast in order to prevent degradation of the samples at elevated temperatures.

For transmission electron microscopy (TEM), thin sections ($\sim 70\text{ nm}$) of PS-*block*-P4VP(PDP)_{1.0} were microtomed at room temperature using a Leica Ultracut UCT-ultramicrotome and a Diatome diamond knife. More hygroscopic PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} samples were cryomicrotomed at $T = -100\text{ }^{\circ}\text{C}$. Sections were picked up onto 600-mesh copper grids, and to enhance contrast, the microtomed sections were stained for 2–3 h in vapors of I_2 crystals, which selectively stains the P4VP domains. Bright-field TEM was performed on FEI Tecnai 12 transmission electron microscope operating at an accelerating voltage of 120 kV. To study the high-temperature structures, the samples were first heated to $T = 170\text{ }^{\circ}\text{C}$ or $T = 210\text{ }^{\circ}\text{C}$ and thereafter rapidly quenched to ca. $T = -180\text{ }^{\circ}\text{C}$ using liquid propane. This procedure “freezes” the high-temperature structures and allows the structure determination with TEM at room temperature.

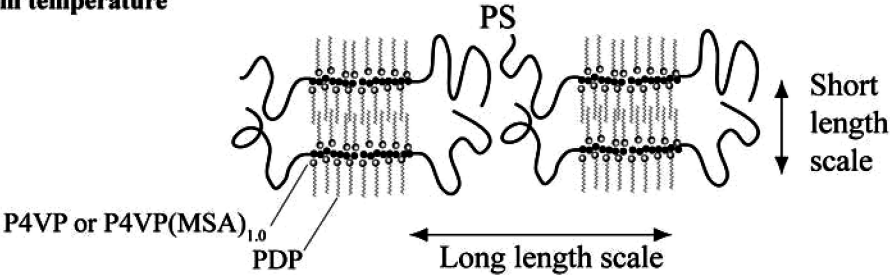


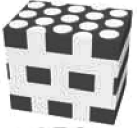




Results and Discussion

PS-*block*-P4VP(PDP)_{1.0} System. First the structure of PS-*block*-P4VP(PDP)_{1.0} is discussed at room temperature. As shown already before by FTIR and structural studies for some compositions and morphologies,^{26,34,35} a dense set of alkyl side chains due to alkylphenols can be bonded to P4VP by simple phenol/pyridine hydrogen bonds (see Scheme 1) to form a

supramolecular comblike architecture within the P4VP block (see Scheme 2). To achieve self-assembly due to such a comblike architecture, sufficient repulsion is required between the polar backbone and the nonpolar alkyl tails where the repulsion can be tailored by selecting the length of the alkyl tail: 12 methyl units do not suffice for self-assembly, whereas 23 methyl units lead to excessive repulsion and easily cause macroscopic phase separation. Therefore, 15 methyl units, i.e., PDP, is known to be a particularly feasible compromise to allow self-assembly at the nanometer length scale upon hydrogen bonding to P4VP.³⁴

The room temperature structures were determined using TEM and SAXS. A comprehensive set of micrographs is presented in the Supporting Information. As a specific example, Figure 1a shows that PS-*block*-P4VP(PDP)_{1.0} with the P4VP(PDP)_{1.0} weight of fraction of 0.62 forms a gyroid structure consisting of the PS and P4VP(PDP)_{1.0} domains having the periodicity at the tens of nanometers length scale. This is supported by SAXS which shows the first intensity maximum at $q^* = 0.018\text{ }^{\circ}\text{Å}^{-1}$, and the higher order reflections at $\sqrt{(4/3)}q^*$, $\sqrt{(7/3)}q^*$, $\sqrt{(10/3)}q^*$, $\sqrt{(19/3)}q^*$, $\sqrt{(20/3)}q^*$ and $\sqrt{8}q^*$ (see Figure 2). Smaller structures within the P4VP(PDP)_{1.0} domains were not resolved by TEM. However, SAXS shows a relatively narrow reflection at $q^* = 0.17\text{ }^{\circ}\text{Å}^{-1}$ at room temperature for this composition (see inset of Figure 2) as well as for compositions of Table 1 (see Supporting Information Figure S1a). A second-order reflection at $2q^*$ is faintly visible for the compositions with the largest P4VP block volume fractions (Supporting Information Figure S1a) but is not observed for the compositions where P4VP is the minority component. Still the small structures can be assigned to be lamellar with a periodicity of $37\text{ }^{\circ}\text{Å}$ due to the following arguments. The small size of the structures and the lack of contrast due to low electron density difference make the TEM challenging, but in some cases the small structures have been directly resolved: They have been resolved by TEM for the homopolymer with slightly longer alkylphenol, i.e., nonadecylphenol, to be lamellar,³⁹ and in high molecular weight PS-*block*-P4VP(PDP)_{1.0} with the P4VP(PDP)_{1.0} weight fraction of 0.45 it has been resolved to be lamellar and perpendicular to the large structure.³⁴ In the case of nonadecylphenol, the small structure has been resolved in a wide range of compositions and has been observed to be lamellar and perpendicular to the large structure.³⁵ Therefore, we conclude that the compositions of Table 1 show diblock copolymer length scale structures and shorter length scale lamellar structures within the P4VP(PDP)_{1.0} domains, i.e., show hierarchical order at room temperature and

Scheme 2. Morphologies, Symbols, and Abbreviations Used in Present Work for PS-*block*-P4VP(PDP)_{1,0} and PS-*block*-P4VP(MSA)_{1,0}(PDP)_{1,0}^a

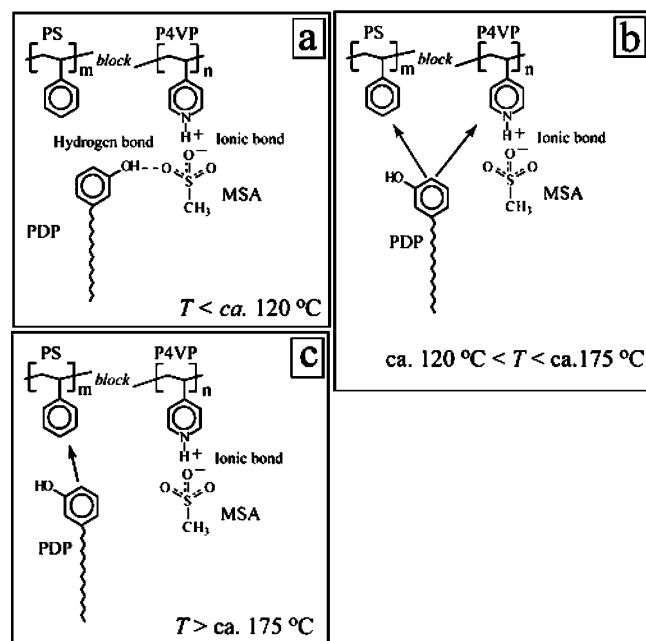
Mechanism for hierarchy at room temperature			
			
Morphology	Symbol	Abbreviation	Description
	●	<i>lam-in-SPH'</i>	Short length scale lamellar order (<i>lam</i>) within a long length scale order consisting of spherical P4VP-containing domains in PS matrix (<i>SPH'</i>).
	△	<i>lam-in-CYL'</i>	Short length scale lamellar order (<i>lam</i>) within a long length scale order consisting of cylindrical P4VP-containing domains in PS matrix (<i>CYL'</i>).
 <p>Note: Small structure not drawn</p>	◆	<i>lam-in-HPL'</i>	Short length scale lamellar order (<i>lam</i>) within a long length scale order consisting of hexagonally perforated P4VP-containing domains in PS matrix (<i>HPL'</i>).
	□	<i>lam-in-LAM</i>	Short length scale lamellar order (<i>lam</i>) of alternating PDP and P4VP or P4VP(MSA) _{1,0} layers within a long length scale lamellar order consisting of alternating P4VP-containing and PS layers (<i>LAM</i>).
 <p>Note: Small structure not drawn</p>	★	<i>GYR-in-lam</i>	Gyroid structure (<i>GYR</i>) at a long length scale where there is a short length scale lamellar (<i>lam</i>) order within P4VP(PDP) _{1,0} or P4VP(MSA) _{1,0} (PDP) _{1,0} due to alternating P4VP and PDP layers.
	▲	<i>CYL-in-lam</i>	Self-assembled PS cylinders (<i>CYL</i>) at a long length scale within a matrix, which forms a short length scale lamellar (<i>lam</i>) order of alternating PDP and P4VP or P4VP(MSA) _{1,0} layers.
	○	<i>SPH-in-lam</i>	Self-assembled PS spheres (<i>SPH</i>) at a long length scale within a matrix, which forms a short length scale lamellar (<i>lam</i>) order of alternating PDP and P4VP or P4VP(MSA) _{1,0} layers.
<p>Note: In <i>lam-in-HPL'</i> and <i>GYR-in-lam</i> the small length scale structure is not drawn as the relative orientation of the small and large length scale structures is not yet known.</p>			

^a The block copolymer length scale structures (long length scale) are due to self-assembly of PS-*block*-P4VP and its complexes and mixtures with PDP and MSA, and the corresponding structures are denoted with capital letters. The prime symbol (') refers to structures where PS forms the matrix. The short length scale structures can be formed within the P4VP(PDP)_{1,0} or P4VP(MSA)_{1,0}(PDP)_{1,0} domains due to self-assembly caused by the pentadecyl combs, and only lamellar structure is observed. This small structure due to the comblike block is denoted with small letters (*lam*).

that the small structure is expected to be perpendicular^{26,34,35} to the large structure. The observed morphologies, symbols, and abbreviations used in present work are schematically represented and explained in Scheme 2. Figure 3 shows the morphology diagram at room temperature. The following hierarchical structures were observed at room temperature: spherical (*lam*-

in-SPH', *SPH-in-lam*), cylindrical (*lam-in-CYL'*, *CYL-in-lam*), gyroid (*GYR-in-lam*), lamellar (*lam-in-LAM*), and hexagonally perforated layer (*lam-in-HPL'*) (the prime symbol (') refers to structures where PS is matrix). The relative orientation of the smaller length scale structure within the comb block domains cannot be concluded for the *lam-in-HPL'* and *GYR-in-lam*

Scheme 3. Schematics of the Interactions in PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0}^a



^a (a) At room temperature, PDP is hydrogen bonded to MSA, which is ionically attached to P4VP. Upon heating the hydrogen bonds are gradually broken. (b) At ca. 120 °C < T < ca. 175 °C PDP is soluble in both PS and P4VP(MSA)_{1.0}. (c) At temperature T > ca. 175 °C PDP is expelled from P4VP(MSA)_{1.0} and becomes a selective solvent for PS. Ultimately, at still higher temperatures PDP becomes miscible in P4VP(MSA)_{1.0}, as was suggested in ref 26.

morphologies. The boundaries between different morphologies are sketched with dashed lines in Figure 3. The lam-in-HPL' and GYR-in-lam morphologies were observed only with the low molecular weight samples, and the morphology diagram is slightly asymmetric, as the lam-in-CYL' region is narrower than the CYL-in-lam region. This is not surprising as some kind of asymmetry was expected given the asymmetric nature between the comb-shaped P4VP(PDP)_{1.0} and coiled PS blocks. In addition, for the high molecular weight samples, strongly enhanced preference for the lam-in-SPH' morphology was observed. Similar behavior of enhanced stability of spherical phases has been previously reported with side-chain liquid crystalline diblock copolymers.^{40,41} Finally, we would like to point out that the lam-in-HPL structure was repeatedly observed despite careful annealing. At present, we cannot conclusively determine whether it is a very long-lived metastable state or equilibrium structure.

Upon heating PS-*block*-P4VP(PDP)_{1.0}, an order-disorder transition of the internal structure within the P4VP(PDP)_{1.0} domains is observed at ca. T = 60 °C (see inset of Figure 2 and the Supporting Information Figure S1b), and the strength of the hydrogen bonds between PDP and P4VP gradually decreases upon further heating.⁴² At ca. T > 120 °C PDP becomes soluble in PS, and it can diffuse also into the PS domains. Therefore, PDP can be located both in the PS and P4VP domains, which essentially increases the relative weight fraction of the PS containing domain. Order-order transitions are therefore expected. A specific example deals S62.83k.P (see Table 1 and Figures 1 and 2), which forms GYR-in-lam morphology at room temperature. Upon heating a sequence of transitions is observed: First, an order-disorder transition of the smaller length scale structure occurs at ca. T = 60 °C. Further heating causes an order-order transition from a gyroid

to a lamellar structure at the larger length scale (Figure 1b) and finally to the HPL' morphology. HPL' structure is clearly manifested in the TEM images showing the projections parallel and normal to the perforated layers (Figure 1c). The dark spots (e.g., Figure 1c; region A) result from the parallel projection to the perforated layer of P4VP(PDP)_{1.0}, and the hexagonal packing of the bright spots (e.g., Figure 1c; region B) results from the normal projection of the hexagonal perforations of the PS domain. The transitions can also be followed using SAXS, and the intensity patterns at different temperatures are shown in Figure 2. At room temperature, reflections corresponding to gyroid structure are observed, as already discussed. At ca. T = 170 °C the reflections of the gyroid structure disappear, and a new intensity pattern characteristic for a lamellar structure is observed (indicated with arrows in the uppermost intensity pattern).

Also, several other sequences of order-order transitions were observed for PS-*block*-P4VP(PDP)_{1.0}, such as the lam-in-LAM \leftrightarrow LAM \leftrightarrow HPL' and SPH-in-lam \leftrightarrow SPH \leftrightarrow CYL \leftrightarrow HPL (see the Supporting Information). A morphology diagram at different temperatures is shown in Figure 4. All samples exhibit at least two thermoreversible order-order transitions, and some of them show even four consecutive ordered phases upon heating and cooling (for reversibility of the transitions, see Supporting Information Figure S4). Phase boundaries at different temperatures are sketched with dashed lines based on the observation using TEM and SAXS. Note that in the diagram the weight fraction of supramolecular comblike block P4VP(PDP)_{1.0} is indicated on the basis of nominal room temperature compositions. The above-described order-order transitions for S62.83k.P (Figures 1 and 2) are indicated with arrows in Figure 4. At high temperature the HPL' structure was observed in a much wider region of the morphology diagram than at room temperature. This is not surprising as the thermally induced phase transition from lamellar to cylinders phase often goes through a long-lived metastable HPL phase.^{21,43-46} Cylindrical structures (CYL') were not observed at T = 170 °C, and for example S28.50k.P with $f_{\text{comb},1}$ = 0.28 formed a spherical structure at elevated temperature, indicating that cylindrical structure probably occurs only in a narrow temperature window. For S63.154k.P with $f_{\text{comb},1}$ = 0.63, the CYL' was observed at T = 210 °C, although other samples even with lower $f_{\text{comb},1}$ formed HPL' structure. Furthermore, the high molecular weight samples showed strongly enhanced preference for the spherical morphology at elevated temperature, and due to their higher polydispersity they are not included in the morphology diagram represented in Figure 4.

In conclusion, the phase behavior of PS-*block*-P4VP(PDP)_{1.0} is complex but can be qualitatively rationalized by some simple arguments. It can be first regarded as a diblock copolymer between PS and P4VP(PDP)_{1.0} where the structure depends on their relative weight fractions. But whereas in the classic diblock copolymers the weight fraction is fixed by synthesis, in PS-*block*-P4VP(PDP)_{1.0} it depends dynamically on the temperature. This can qualitatively be understood by classic polymer solvent phase behavior where polymers become miscible in nonaqueous solvents at high temperature and phase separate to two-phase system by lowering the temperature. In the present case, the phenol-pyridine hydrogen bonding leads to miscibility of P4VP in PDP at all practical temperatures whereas heating to T = ca. 120 °C is required to achieve miscibility of PDP in PS. Therefore, the phase balance of the block copolymer is changed: for T < ca. 120 °C, PDP is mainly located in the P4VP domains whereas for T > ca. 120 °C it can be located

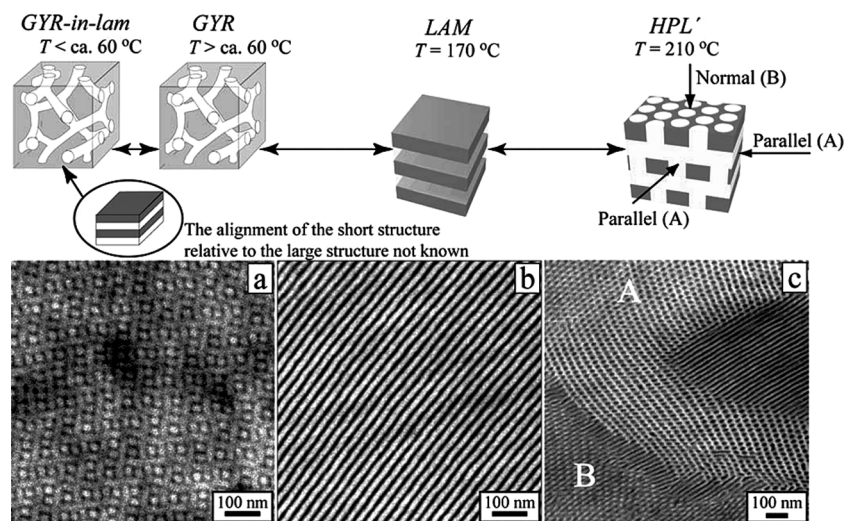


Figure 1. TEM micrographs of PS-*block*-P4VP(PDP)_{1.0} with the P4VP(PDP)_{1.0} weight fraction 0.62 (sample S62.83k.P). (a) At room temperature a GYR-in-lam structure is formed. At ca. $T = 60\text{ }^{\circ}\text{C}$ the lam structure within P4VP(PDP)_{1.0} undergoes an ODT, and only the GYR structure remains. (b) At $T = 170\text{ }^{\circ}\text{C}$ a LAM structure was observed and (c) a HPL' at ca. $T = 210\text{ }^{\circ}\text{C}$. The normal and parallel projections of the HPL' structure are illustrated. The P4VP-containing domains appear dark in the images due to the I₂ staining. Note that the gyroid morphology in (a) also contains a smaller length scale structure within P4VP(PDP)_{1.0} domains, which was not resolved in TEM but is indicated by the SAXS measurements.

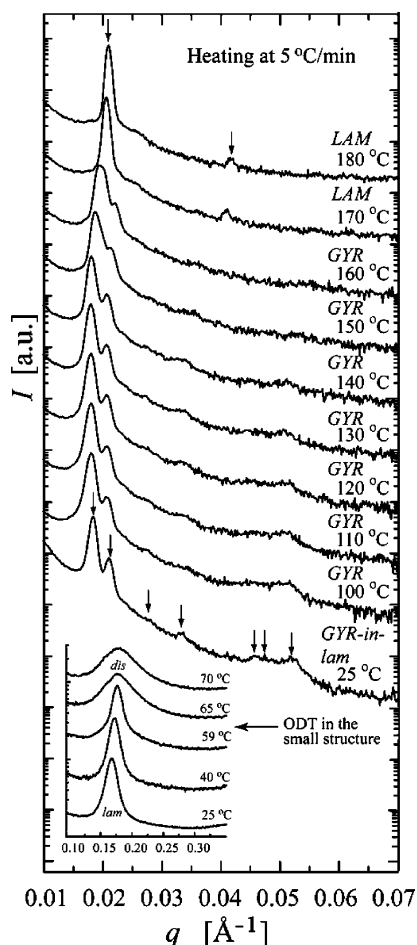


Figure 2. SAXS intensity patterns of PS-*block*-P4VP(PDP)_{1.0} with the P4VP(PDP)_{1.0} weight fraction 0.62 (sample S62.83k.P) as a function of temperature, indicating a gyroid to lamellar transition at the block copolymer length scale and lamellar to disorder transition in an order of magnitude smaller length scale. The curves have been measured using a heating rate $5\text{ }^{\circ}\text{C}/\text{min}$.

both in P4VP- and PS-containing domains. This causes transitions to new structures. In addition, because of the comblike architecture of P4VP(PDP)_{1.0}, the small length scale lam structure and related ODT to disordered state is observed.

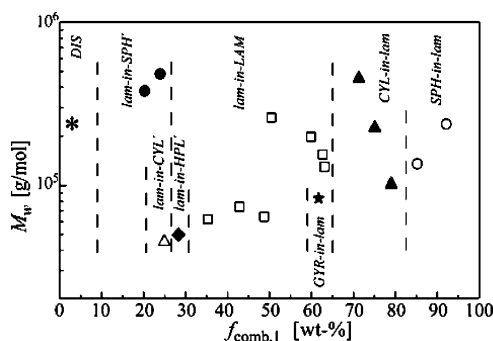


Figure 3. Morphology diagram of PS-*block*-P4VP(PDP)_{1.0} as a function of the weight fraction of the comblike block P4VP(PDP)_{1.0} ($f_{\text{comb},1}$) at room temperature. M_w refers to the nominal total molecular weight of the PS-*block*-P4VP(PDP)_{1.0} supramolecule. The prime symbol refers to the case where PS forms the matrix. For the morphologies, symbols, and abbreviations see Scheme 2.

Altogether, PS-*block*-P4VP(PDP)_{1.0} constitutes an example of how a diblock copolymer phase behavior can be combined to classic polymer-solvent or polymer-plasticizer phase behavior with elevated temperature miscibility to achieve complex phase transition sequences. We still also emphasize that the notion PS-*block*-P4VP(PDP)_{1.0} just refers to the nominal stoichiometry when prepared, as the actual location of PDP depends on the temperature and kinetics.

PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} System. We next discuss PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} (see Scheme 3) where the original aim was twofold: first to provide charged blocks due to salt formation with pyridine/sulfonic acid salts and to use sulfonate/phenol hydrogen bonds instead of pyridine/phenol to bond PDP. Ultimately, it turned out that, among different sulfonic acids, methanesulfonic acid (MSA) renders particularly interesting temperature induced phase separation²⁶ to be discussed also here in some detail. The pyridines of the P4VP block are first stoichiometrically protonated with MSA (see Supporting Information for the FTIR data). The ionic interaction between P4VP and MSA is strong, and FTIR shows that it remains unchanged upon heating to all practical temperatures (see Supporting Information Figure S9). The aimed hydrogen bonding between sulfonates and PDP to form a comblike P4VP-(MSA)_{1.0}(PDP)_{1.0} block is shown in Scheme 3. Because of the

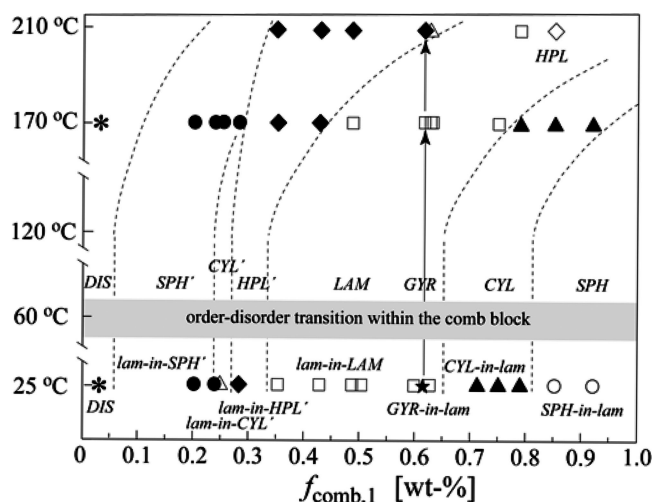


Figure 4. Morphology diagram for PS-*block*-P4VP(PDP)_{1.0} as a function of the weight fraction of comblike block P4VP(PDP)_{1.0} ($f_{\text{comb},1}$) at different temperatures. The prime symbol refers to structures where PS forms the matrix. Note that $f_{\text{comb},1}$ is based on the nominal room temperature composition. For the morphologies, symbols, and abbreviations see Scheme 2.

complicated FTIR bands at 1200–1300 cm^{-1} relevant for the sulfonates, it has turned difficult to directly investigate the hydrogen bonding between the sulfonates and phenols, and the feasibility of the hydrogen bond has to be assessed only indirectly on the basis of observed structures and related oligomeric supramolecular crystals.^{26,31,47} The hydrogen bonding between the sulfonates of MSA and PDP is expected to be substantially weaker and gradually broken upon heating.

The studied PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} samples and their morphologies are listed in Table 2, and the denotations for the structures are shown in Scheme 2. (The weight fraction of supramolecular comblike block P4VP(MSA)_{1.0}(PDP)_{1.0} $f_{\text{comb},2}$ ranges from 0.29 to 0.88 at room temperature.) The morphology was characterized using TEM and SAXS, and the Supporting Information gives a selection of TEM micrographs. As a specific example, TEM indicates that at room temperature PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with $f_{\text{comb},2} = 0.40$ (S40.67k.MP) shows a lamellar structure (LAM) (see Figure 5a). Smaller structures were not resolved with TEM. SAXS (see Figure 6) shows at room temperature the first intensity maximum at $q^* = 0.0177 \text{ \AA}^{-1}$, and the higher order reflections are at $2q^*$, $3q^*$, $4q^*$, $5q^*$, and $6q^*$ characteristic for a lamellar structure with the periodicity of 35.5 nm. At higher scattering angles SAXS shows a distinct reflection at $q = 0.13 \text{ \AA}^{-1}$ for all of the P4VP(MSA)_{1.0}(PDP)_{1.0} samples (inset of Figure 6 and Supporting Information Figure S1c), but higher order reflections have not been conclusively observed. Still, on the basis of indirect arguments on the volumes of the molecules and the related compositions in P4VP(PDP)_{1.0}, we can fairly convincingly address the structure to be lamellar. Therefore, we address the structure of Figures 5 and 6 as lam-in-LAM. The room temperature structures are collected in Figure 7 as a function of $f_{\text{comb},2}$ (see also Supporting Information and Figures 6 and 7). The morphology diagram is also in this case asymmetric, as the CYL-in-lam was observed even for a very high weight fraction of the comb domain ($f_{\text{comb},2} = 0.88$). Hexagonally perforated layer and gyroid structures were not observed for these samples at room temperature. Also in this system, a strong preference of the lam-in-SPH' was observed (see the high molecular weight sample S35.297k.MP with $f_{\text{comb},2} = 0.35$).

We will next address the phase transitions of a wide range of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} as a function of temperature

based on SAXS and TEM. As a characteristic example, PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with the P4VP(MSA)_{1.0}(PDP)_{1.0} weight fraction of 0.40 (sample S40.67k.MP) at various temperatures is discussed. At room temperature TEM shows at the block copolymer length scale LAM structure (Figure 5a) at $T = 170 \text{ °C}$ CYL' structure (Figure 5b) and at $T = 210 \text{ °C}$ a SPH' structure (Figure 5c), suggesting that order–order transitions take place at this length scale. As already described, the structure is lam-in-LAM based on SAXS (Figure 6). The order–disorder transition of the smaller length scale structure within comblike block occurs at ca. $T = 125 \text{ °C}$ (see Supporting Information Figure S1b), which leads to LAM order without hierarchies. At ca. $T = 170 \text{ °C}$ the first intensity maximum appears at $q^* = 0.0266 \text{ \AA}^{-1}$ and the higher order reflections at $\sqrt{3}q^*$, $2q^*$, and $\sqrt{7}q^*$ characteristic of a CYL' structure, and at $T = 210 \text{ °C}$ intensity maxima at $q^* = 0.0221 \text{ \AA}^{-1}$, $\sqrt{2}q^*$, $\sqrt{3}q^*$, and $2q^*$ are observed, indicating a SPH' structure. The structures are reversible upon cooling, whereas some hysteresis is usually observed for the moderately rapid temperature sweep rates.

To demonstrate the reversibility of the structures, Figure 8 shows the SAXS intensity patterns for PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with the $f_{\text{comb},2} = 0.56$ (sample S56.44k.MP) at different temperatures upon heating and cooling (heating rate 5 °C/min and cooling rate 10 °C/min), indicating reversibility of the transitions with some hysteresis. At room temperature a LAM structure is observed with the first intensity maximum at $q^* = 0.028 \text{ \AA}^{-1}$, and the higher order reflections are at $2q^*$ and $3q^*$. At $T = 170 \text{ °C}$ it forms a CYL' structure with first intensity maximum at $q^* = 0.038 \text{ \AA}^{-1}$ and the higher order reflections at $\sqrt{3}q^*$ and $2q^*$, and at $T = 200 \text{ °C}$ intensity maxima at $q^* = 0.032 \text{ \AA}^{-1}$, $\sqrt{2}q^*$, $\sqrt{3}q^*$, and $2q^*$ are observed indicating a SPH' structure. The structures are recovered upon cooling showing the reversibility of the transitions. However, in Figure 8 the peaks are not as pronounced under cooling as under heating due to the faster cooling rate.

The observed order–order transitions at different temperatures for PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} are collected in Figure 9. Also in this system several thermoreversible order–order transitions are observed; even five consecutive ordered phases for some of the samples upon heating and cooling (for reversibility of the transitions, see Figure 8 and Supporting Information Figure S13). For instance, S48.81k.MP with $f_{\text{comb},2} = 0.48$ forms lam-in-LAM structure at room temperature, and an order–disorder transition of the smaller length scale structure occurs at ca. $T = 125 \text{ °C}$. Further heating induces OOTs from a lamellar to a HPL' to a CYL' and finally to a SPH' structure. The morphology diagram at room temperature is slightly asymmetric, as being shifted toward the high $f_{\text{comb},2}$ side of the diagram. For example, at room temperature CYL-in-lam morphology was observed even for very high values $f_{\text{comb},2} = 0.88$, although in simple diblock copolymers the spherical structures would have been expected. It should be noted that at high $f_{\text{comb},2} = 0.88$ and 0.82 , i.e., for S88.161k.MP and S82.121k.MP, the cylinders in the lamellar matrix were mainly short wormlike cylinders, i.e., showed poor overall order. Most of the studied samples formed a lam-in-LAM structures at room temperature, and upon heating they first undergo an order–disorder transition of the smaller length scale structure within P4VP(MSA)_{1.0}(PDP)_{1.0} domains followed by an order–order transition to CYL' and still another transition to SPH' at elevated temperatures. In some samples the transition from lamellar to cylindrical structure occurred through HPL' ($f_{\text{comb},2} = 0.54, 0.67$, and 0.48 , i.e., S54.71k.MP, S67.95k.MP, and S48.81k.MP).

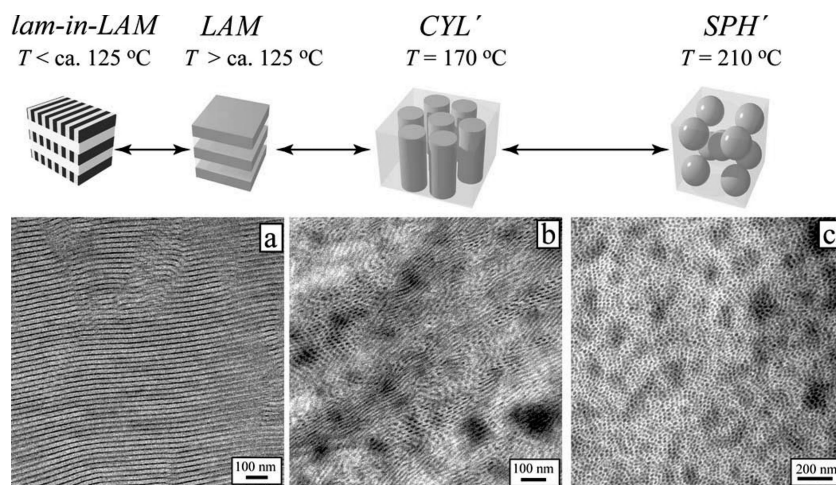


Figure 5. TEM micrographs of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with the comblike block P4VP(MSA)_{1.0}(PDP)_{1.0} weight fraction $f_{\text{comb},2} = 0.40$ (sample S40.67k.MP) (a) at room temperature showing a lam-in-LAM structure. Note that the smaller lam structure within the P4VP(MSA)_{1.0}-(PDP)_{1.0} domains was not resolved in TEM but can be inferred from SAXS and analogical compositions. At $T = 125$ °C the smaller length scale lam structure of P4VP(MSA)_{1.0}(PDP)_{1.0} has an ODT. (b) CYL' was observed at $T = 170$ °C and (c) SPH' at $T = 210$ °C. P4VP shows dark in the images due to the I₂ staining.

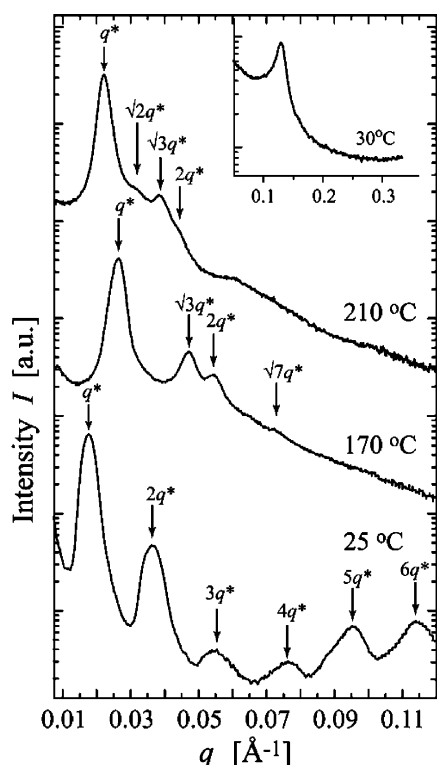


Figure 6. SAXS intensity patterns for PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with the $f_{\text{comb},2} = 0.40$ (sample S40.67k.MP). The curves have been measured upon heating 5 °C/min and show characteristic reflections for LAM, CYL', and SPH' structures. The SAXS curve corresponding to the smaller length scale structure within supramolecular comblike P4VP(MSA)_{1.0}(PDP)_{1.0} at $T = 30$ °C is shown in the inset, whereas at $T = 170$ °C and $T = 210$ °C no distinct reflections are observed due to ODT.

All of the studied compositions of PS-*block*-P4VP(MSA)_{1.0}-(PDP)_{1.0} lead to spherical structures at high temperature which is a manifestation of distinct phenomenon related to polymer-solvent systems concerning the P4VP(MSA)_{1.0} and PS with PDP. Near room temperature PDP is miscible in P4VP(MSA)_{1.0} and poor solvent for PS and therefore predominantly observed in the P4VP(MSA)_{1.0} block. Heating past $T = \text{ca. } 120$ °C causes PDP to become a solvent for PS, and therefore PDP is miscible in both PS and P4VP(MSA)_{1.0}. But passing ca. $T = 175$ °C PDP becomes immiscible in P4VP(MSA)_{1.0} still remaining a

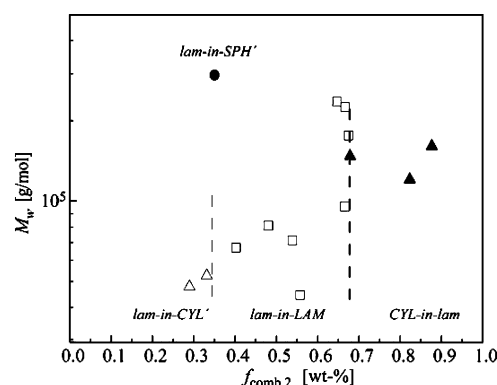


Figure 7. Morphology diagram of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} as a function of weight fraction of the supramolecular comb block P4VP(MSA)_{1.0}(PDP)_{1.0} ($f_{\text{comb},2}$) at room temperature. M_w refers to the molecular weights of the supramolecules, including both MSA and PDP. The prime symbol refers to the phases where PS forms the matrix. For the morphologies, symbols, and abbreviations see Scheme 2.

solvent for PS, leading to an expulsion of PDP predominantly to the PS domains. This drastically enhances the effective relative volume fraction of the PS-containing block. For instance, the calculated weight fractions of the PS domain at room temperature range from $f_{\text{comb},2} = 0.88$ (S88.161k.MP) to $f_{\text{comb},2} = 0.29$ (S29.48k.MP), whereas at temperature above $T = 175$ °C, when PDP is found predominantly in the PS domains, the weight fractions between $f_{\text{comb},2} = 0.35$ and $f_{\text{comb},2} = 0.12$, respectively, are expected. This leads to a spherical morphology at the elevated temperature ($T = 210$ °C) for all samples. Both the asymmetric phase behavior and solvent behavior of PDP affect the morphology diagram of PS-*block*-P4VP(MSA)_{1.0}-(PDP)_{1.0}, and therefore it is considerably different from the morphology diagram of the PS-*block*-P4VP(PDP)_{1.0} system.

Conclusion

A series of polymeric comb-coil supramolecules constituting of diblock copolymers with hydrogen-bonded low molecular weight amphiphilic compounds with pentadecyl tails and phenolic end groups were investigated on the basis of PS-*block*-P4VP(PDP)_{1.0} and PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} using different block lengths. Morphologies at different temperatures were determined by TEM and SAXS. At room temperature they contain a structure-in-structure hierarchy, where the large length

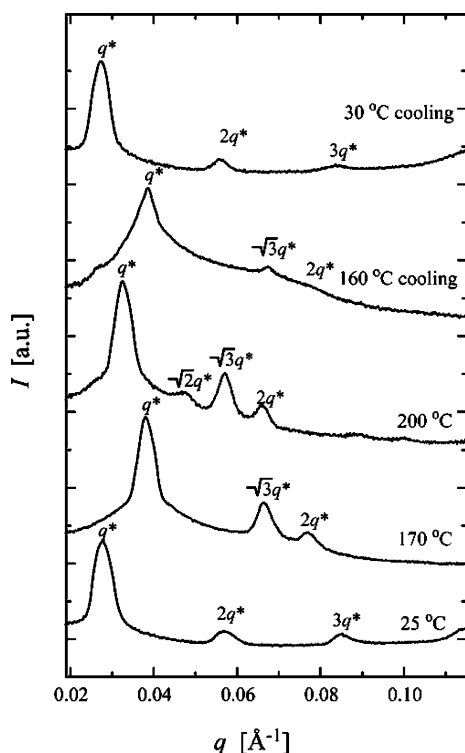


Figure 8. SAXS intensity patterns at different temperatures for PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} with the $f_{\text{comb},2} = 0.56$ (sample S56.44k.MP) showing LAM, CYL', and SPH' structures upon heating and recovery of the structures upon cooling.

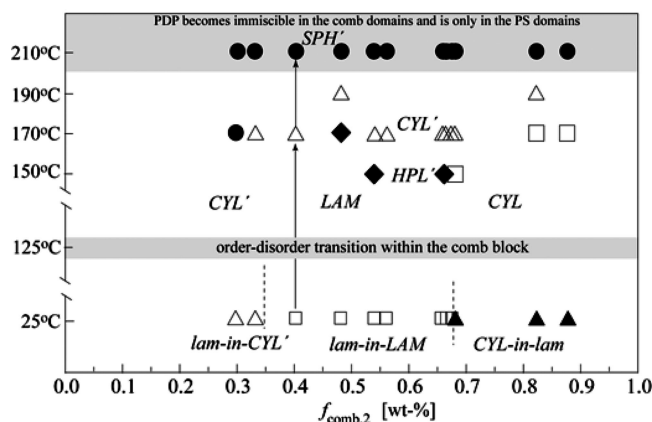


Figure 9. Morphology diagram of PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} as a function of weight fraction of the comb block ($f_{\text{comb},2}$) at different temperature. The prime symbol refers to structures where PS is matrix. Note that $f_{\text{comb},2}$ is based on the room temperature nominal compositions. For the morphologies, symbols, and abbreviations see Scheme 2.

scale spherical (SPH), cylindrical (CYL), lamellar (LAM), hexagonal perforated layer (HPL), or gyroid (GYR) structure corresponds to the block copolymer and the short length scale lamellar structure (lam) results from the repulsive pentadecyl side chains of PDP hydrogen bonded to the P4VP or P4VP-(MSA)_{1.0} chains to form the supramolecular comb block.

In the case of PS-*block*-P4VP(PDP)_{1.0}, PDP is mainly located in the P4VP domains at room temperature due to the pyridine/phenol hydrogen bond. The morphology diagram is slightly asymmetric, for example, the lam-in-CYL' (lamellar P4VP/PDP internal order in cylindrical domains within PS matrix) phase region being narrower than CYL-in-lam (cylindrical PS domains in lamellar matrix of alternating P4VP and PDP layers). Upon heating, several thermoreversible transitions were observed: First, the smaller length scale lam structure within P4VP(PDP)_{1.0}

has an order–disorder transition at ca. $T = 60$ °C. Further heating past $T = \text{ca. } 120$ °C causes PDP to be a miscible (solvent) also for the PS, leading to increase in the effective volume of PS containing domain, which in turn causes order–order transitions of the block copolymer structure. Reversible phase transition sequences are reported that are not possible only by changing the Flory–Huggins interaction parameter χ by temperature. For example, an order–order transition from lam-in-HPL' to SPH' morphology was observed. An additional note in the morphology diagram is that HPL' morphology was repeatedly observed on a surprisingly wide region at elevated temperature for PS-*block*-P4VP(PDP)_{1.0} samples, whereas the cylindrical structure (CYL') occurred only in a narrow range. New morphologies are also introduced: GYR-in-lam and lam-in-HPL' (where PS and P4VP(PDP)_{1.0} form either gyroid or HPL structures and the latter domain has an additional internal lam structure due to alternating P4VP and PDP layers).

In PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} the comb-shaped block is formed due to the sulfonate/phenol hydrogen bond, the backbone is charged, and the phase behavior is more complex. At room temperature lam-in-CYL' (alternating lamellae of P4VP(MSA)_{1.0} and PDP within cylinders in PS matrix), lam-in-LAM (alternating lamellae of P4VP(MSA)_{1.0} and PDP within alternating lamellae of P4VP(MSA)_{1.0}(PDP)_{1.0} and PS), and lam-in-CYL (PS cylinders in a matrix consisting of alternating lamellae of P4VP(MSA)_{1.0} and PDP) structures were observed at room temperature. Heating caused several consecutive thermoreversible order–order transitions: First an ODT of the smaller length scale structure within P4VP(MSA)_{1.0}(PDP)_{1.0} domains occurs at ca. $T = 125$ °C, and PDP becomes miscible in PS. In this case PDP is observed in both P4VP(MSA)_{1.0} and PS domains. But curiously, at $T = \text{ca. } 175$ °C PDP becomes nonsolvent of P4VP(MSA)_{1.0} and is expelled predominantly to PS. This has a drastic effect on the phase balance and on the structures. In some samples even five consecutive ordered phases were observed upon heating and cooling, such as (lam-in-LAM) \rightleftharpoons LAM \rightleftharpoons HPL' \rightleftharpoons CYL' \rightleftharpoons SPH' (S67.95k.MP, S54.71k.MP, and S48.81k.MP) and (CYL-in-lam) \rightleftharpoons CYL \rightleftharpoons LAM \rightleftharpoons CYL' \rightleftharpoons SPH' (S82.121k.MP) (Figure 9). Above $T = 200$ °C only spherical morphology (SPH') was observed.

The results can suggest generalization, as PDP can also be regarded as a solvent molecule that remains as an integral part of the composition, i.e., a plasticizer. This work discusses how self-assembly (linear block copolymer and comb-shaped supramolecular architectures) and polymer/plasticizer phase behavior can be combined to design responsive complex materials. As e.g. order–order transitions of lamellar-in-lamellar structure have been shown to lead electrically²⁶ and optically³¹ responsive materials, the new observed morphologies and several consecutive transitions of supramolecular comb–coil diblock copolymers may lead to new type of functional materials.

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Supporting Information Available: Representation of several order–order transitions for a series of PS-*block*-P4VP(PDP)_{1.0} and PS-*block*-P4VP(MSA)_{1.0}(PDP)_{1.0} samples based on TEM, SAXS, and FTIR experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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