

Random Copolymer Effect in Self-Assembled Hydrogen-Bonded P(S-*co*-4VP)(PDP) Side-Chain Polymers

Joost de Wit,[†] Gert Alberda van Ekenstein,[†] Evgeny Polushkin,[†] Juuso Korhonen,[‡] Janne Ruokolainen,^{*,‡} and Gerrit ten Brinke^{*,†}

Laboratory of Polymer Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, and Department of Applied Physics and Center for New Materials, Helsinki University of Technology, P.O. Box 5100, FIN-02015, TKK, Espoo, Finland

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ABSTRACT: Random copolymers of styrene and 4-vinylpyridine P(S_{1-x}-*co*-4VP_x) were synthesized to study the effect of the random copolymer “repulsion” on the self-assembly in hydrogen-bonded complexes with pentadecylphenol (one PDP molecule per 4VP group). The major trends observed as a function of the fraction of styrene monomers $1 - x$ in the random copolymer are a decrease in order–disorder transition temperature, T_{ODT} , and a decrease in the periodic length scale of the ordered lamellar state. The lower T_{ODT} results from a partial shielding in the disordered state of the highly unfavorable styrene/4-vinylpyridine interactions by the PDP alkyl tails. The reduced layer thickness in the ordered state is due to the relaxation into a more coil-like conformation of the alkyl tails of the PDP amphiphiles, made possible by the presence of styrene units. The self-assembly properties of P(S_{1-x}-*co*-4VP_x)(PDP)_{1,0} are compared with those of the lamellar self-assembled homopolymer-based P4VP(PDP)_x system, where x denotes the number of PDP molecules per 4VP repeat unit. As in P(S_{1-x}-*co*-4VP_x)(PDP)_{1,0}, in P4VP(PDP)_x also only a fraction x of the total number of monomers of the macromolecule may potentially hydrogen bond with PDP molecules at any given instant. In contrast to P(S_{1-x}-*co*-4VP_x)(PDP)_{1,0}, for P4VP(PDP)_x, however, the long period is found to increase for decreasing values of x .

Introduction

In the field of polymer phase behavior, random copolymers play a distinctive role. Chemically different homopolymers usually do not mix due to the tendency for the intermolecular interactions to be unfavorable. Only in the case of specific interactions, notably intermolecular hydrogen bond formation, does miscibility occur.^{1–3} An effective way to create miscible polymer pairs is by letting one of the components be a random copolymer.^{4–6} A striking example involves the miscibility of random copolymers of styrene and acrylonitrile (SAN) with various homopolymers such as poly(vinyl chloride), poly(methyl methacrylate), poly(ϵ -caprolactone), etc.⁷ On mixing of SAN with any of these polymers the number of very unfavorable interactions between styrene and acrylonitrile is reduced to the extent that the enthalpy of mixing may even become negative. Within the solubility parameter approach, the random copolymer composition may be selected in such a way that the value of the solubility parameter of the random copolymer actually coincides with the value of the solubility parameter of the homopolymer component.⁸ The copolymer strategy is not only a well-established method to create miscible polymer blends; it also has been employed in the field of block copolymers. Two examples are the use of block copolymer compatibilizers with one of the blocks being a SAN random copolymer⁹ and the use of a grafted layer of random copolymers of styrene (S) and methyl methacrylate (MMA) to create a neutral substrate for PS-*b*-PMMA diblock copolymers.¹⁰

The specific position taken by SAN in the field of polymer blends is directly related to the very unfavorable S/AN interactions or the large difference in value of the solubility parameter of the corresponding homopolymers PS and PAN. Another polymer couple known for its strongly unfavorable interaction is PS and poly(4-vinylpyridine) (P4VP).^{11–13} A random co-

polymer miscibility study led to an interaction parameter value of $\chi_{S,4VP} \cong 0.34$,¹² a value that was confirmed by a neutron scattering study on PS-*b*-P4VP diblock copolymers.¹³ In the past decades much of our research efforts concerned the self-assembly in hydrogen-bonded side-chain polymers based on P4VP homopolymers and PS-*b*-P4VP diblock copolymers. Self-assembly in poly(4-vinylpyridine)-based hydrogen-bonded side-chain polymers with pentadecylphenol, P4VP(PDP), has been amply studied.^{14–17} On cooling at ca. 67 °C the nominally fully complexed P4VP(PDP)_{1,0} turns from a disordered state into an ordered lamellar state. If a PS-*b*-P4VP diblock copolymer rather than homopolymer P4VP is used in combination with PDP, a hierarchically ordered structure is formed consisting of a PS phase that is microphase separated from the P4VP(PDP) phase. The latter in turn contains below ca. 67 °C the lamellar structure just discussed for pure P4VP(PDP).^{18,19} In the case of PS-*b*-P4VP(PDP) diblock copolymer-based supramolecules, the effect of PDP on the order–disorder transition temperature of the large-length-scale ordering between PS and P4VP(PDP) has not yet been studied systematically. From a study on the molecular weight dependence of the long period of lamellar self-assembled PS-*b*-P4VP(PDP), with one PDP molecule per 4VP repeat unit, we were able to conclude that these systems were, as far as the large-length-scale ordering between PS and P4VP(PDP) is concerned, in the intermediate segregation regime, whereas the corresponding pure PS-*b*-P4VP diblock copolymers were in the strong segregation regime.²⁰ Apparently, the alkyl tails of PDP reduce the number of S/4VP interactions in the interface, thus lowering the interfacial tension in the ordered state as well. In this respect it is also of interest to note that PS and PDP become actually fully miscible at elevated temperatures, above ca. 135 °C.¹⁶

The simplest system to address the effect of PDP on the unfavorable interactions between PS and P4VP is to use P(S-*co*-4VP) random copolymers in combination with PDP and study the order–disorder transition and the ordered state as a function of the copolymer composition. To investigate this, we took

* To whom correspondence should be addressed.

[†] University of Groningen.

[‡] Helsinki University of Technology.

Table 1. Characteristics of the Poly(S-co-4VP) Samples

sample	fraction 4VP (mol %)	M_w (kg/mol)	M_n (kg/mol)	M_w/M_n	T_g (°C)
PS4VP _{56.8}	56.8	64.3	40.1	1.6	130
PS4VP _{70.3}	70.3	71.3	53.9	1.3	138
PS4VP _{81.7}	81.7	167.5	71.5	2.3	143
PS4VP _{84.1}	84.1	234.7	65.4	3.6	145
PS4VP _{91.7}	91.7	110.2	54.5	2.0	150
PS4VP _{96.5}	96.5	164.8	76.0	2.2	153
P4VP	100	61.0	26.0	2.3	142

nominally fully complexed $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ systems and contrasted it with the behavior of the homopolymer-based $P4VP(PDP)_x$ hydrogen-bonded complexes. Here the subscript of PDP denotes the number of PDP molecules per 4VP unit, whereas the subscript of 4VP denotes the random copolymer composition expressed in mole fraction 4VP. In both $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ and $P4VP(PDP)_x$ the same fraction x of monomers of the macromolecules involved may potentially hydrogen bond to a PDP molecule at any given instant. However, for $P4VP(PDP)_x$ the non-hydrogen-bonded groups of the polymer are 4VP units, whereas for $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ the non-hydrogen-bonded groups are largely S units. The effect of styrene on the ODT of $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ confirmed the “copolymer effect”: in the disordered state the number of S/4VP interactions is strongly reduced due to the presence of the alkyl groups, and the transition to the ordered state therefore occurs at a reduced temperature. Also, the observation that the x -dependence of the layer thickness of $P4VP(PDP)_x$ and $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ is essentially opposite is argued to be in line with the different interactions present.

Experimental Section

Materials. Styrene, 4-vinylpyridine, and 3-pentadecylphenol (PDP) were purchased from Aldrich. Styrene and 4-vinylpyridine were purified by vacuum distillation. PDP was recrystallized twice from petroleum ether (40–60 w/w) and dried in vacuum at 40 °C. Azobis(isobutyronitrile) (AIBN) was purchased from Fluka and used as received. Pure poly(4-vinylpyridine) was purchased from Polysciences, Inc., and was used as received.

Poly(S-co-4VP) Synthesis. Copolymers of styrene (S) and 4-vinylpyridine (4VP) were synthesized using AIBN as radical initiator. In a three-necked round-bottom flask equipped with magnetic stirrer, a serum cap, and a N_2 /vacuum inlet, monomer mixtures with varying S/4VP ratios (total weight of monomers is between 5 and 15 g) were dissolved in ca. 50 mL of toluene. The mixtures were then degassed (freeze–thaw method) and heated using an oil bath of 80 °C, after which the polymerization was initiated by adding an amount of degassed solution of AIBN in toluene (ca. 8 mg/mL). The amount of initiator solution added corresponded to a desired molecular weight of the polymers of ca. 50 000 g/mol. The polymerization was terminated after ca. 3 h by adding a small amount of hydroquinone in order to avoid the conversion to exceed 10%, preventing the consequences of drift in the monomer ratio. The copolymers were precipitated twice from toluene into heptane and dried overnight at 40 °C under reduced pressure.

Characterization. Molecular weights of the copolymers were determined by using a Waters gel permeation chromatograph equipped with 2 PL-gel mixed-c columns and a refractive index detector. Dimethylformamide (DMF) with 0.01 M LiBr was used as an eluent, and polystyrene samples were used as calibration standards. The S/4VP ratio in the polymers was determined by elemental analysis conducted on an EA3000 CHNS analyzer (Euro). Glass transition temperatures were recorded on a DSC Q1000 (TA Instruments), using a heating rate of 1 °C/min and a temperature modulation of 0.5 °C/min. The results of the analysis are presented in Table 1.

Sample Preparation. $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ was prepared by dissolving PDP and polymer in chloroform, obtaining a 3 wt %

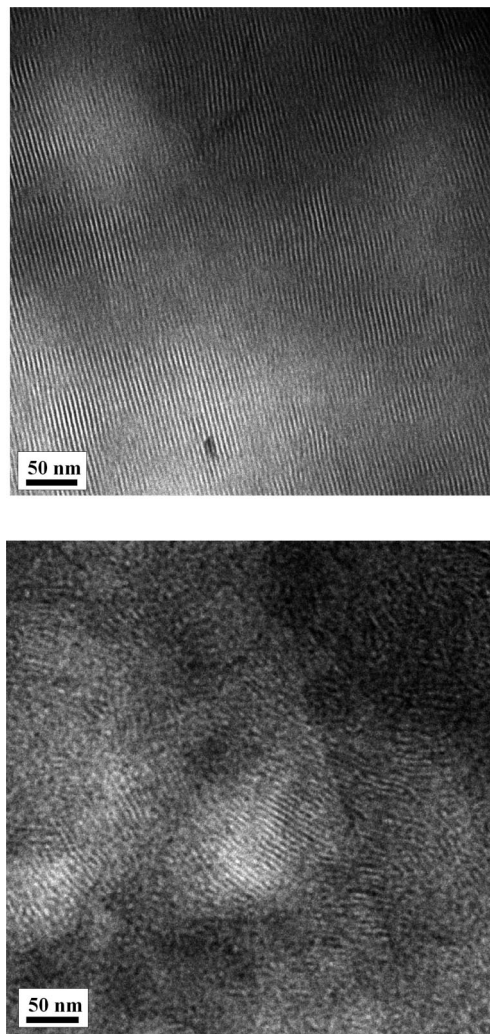


Figure 1. TEM micrographs of iodine-stained $P(S_{1-x}\text{-co-4VP}_x)(PDP)_{1.0}$ complexes for $x = 0.96$ (top) and $x = 0.70$ (bottom).

solution. The solution was poured into a Petri dish and covered in order to allow for slow evaporation of the solvent. After complete evaporation the polymer–amphiphile complex was dried overnight at 40 °C in vacuum.

Analysis. Small-angle X-ray scattering (SAXS) was performed at the DUBBLE Beamline (BM26) at the ESRF in Grenoble, France.²³ The sample–detector distance was ca. 165 cm for SAXS and ca. 4 cm for WAXS; the X-ray wavelength was $\lambda = 1.24$ Å ($E = 10$ keV). A Linkam HFS 191 sample stage was used to heat and cool the sample with a rate of 5 °C/min. The magnitude of the scattering vector, q , is defined as $q = (4\pi/\lambda) \sin \theta$, where θ is half the scattering angle. The measuring time per frame was 30 s, resulting in a 2.5 °C temperature window for each frame.

Polarized optical micrographs were taken on a Zeiss Axiophot equipped with a Mettler FP82HT hot stage and crossed polarizers.

For recording TEM micrographs the bulk samples were sectioned at –60 °C using a Leica Ultracut UCT ultramicrotome and a cryo 25° Diatome diamond knife. Sections with a thickness of ca. 50–70 nm were collected on lacey carbon support film grids. In order to enhance contrast, sections were stained for 20–30 min in vapor of iodine crystals. For the samples with the smallest amount of 4VP, the staining was performed at a reduced temperature of 4 °C. The effect of staining artifacts was studied by varying the staining time from 30 min up to 3 h. Bright-field TEM was performed on a FEI Tecnai 12 transmission electron microscope operating at an accelerating voltage of 120 kV, both cryo and at room temperature. Cryo-TEM studies were performed using a Gatan 910 cryoholder.

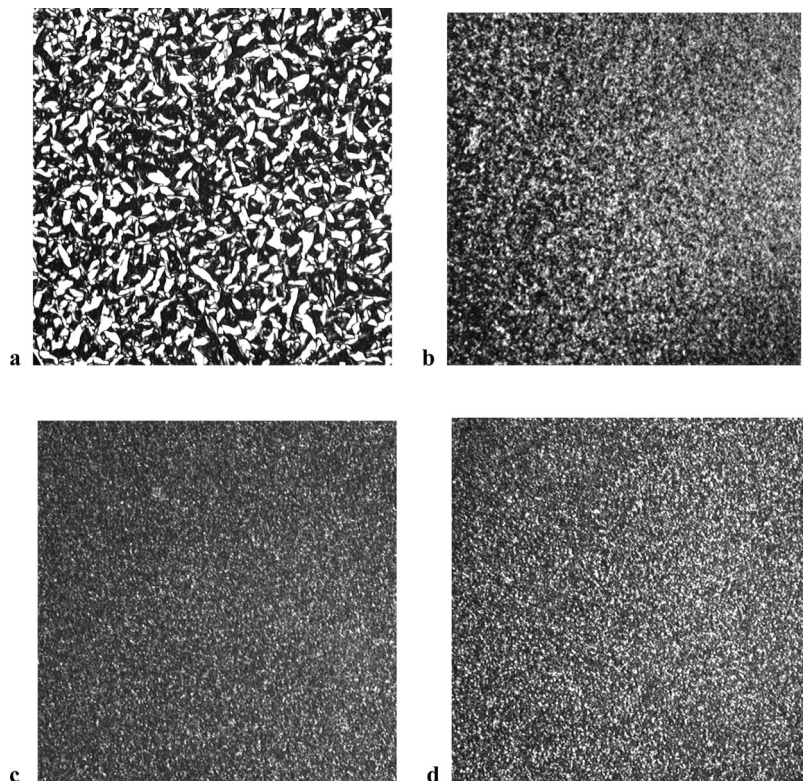


Figure 2. Polarized optical micrographs ($310 \times 310 \mu\text{m}$) of hydrogen-bonded complexes of $\text{P}(\text{S}_{1-x}\text{-co-4VP}_x)(\text{PDP})_{1.0}$ with fractions of 4VP equal to (a) 100%, (b) 96.1%, (c) 92.2%, and (d) 91.7%.

Results and Discussion

It is well-known from previous studies that P4VP(PDP) systems form self-assembled lamellar structures below a certain temperature.^{18,19} SAXS measurements merely show the first-order peak of the ordered structure with sometimes a very weak second-order peak. Below room temperature the alkyl tails of PDP crystallize, and the second-order peak becomes more prominent. The lamellar structure has been verified by TEM—first for the complexes with slightly longer nonadecylphenol amphiphiles¹⁷ but later also for PDP.¹⁸ The near or complete absence of the second-order peak might be due to symmetry, but since it is invariably observed for many different P4VP-based hydrogen-bonded side-chain polymers,²⁴ it is most likely due to the fact that the lamellar (smectic) structure formed has a substantial short-range disorder, a phenomenon that is well-known for the smectic LC phase.^{25,26}

That the self-assembly in the random copolymer-based $\text{P}(\text{S}_{1-x}\text{-co-4VP}_x)(\text{PDP})_{1.0}$ systems investigated here also results in a lamellar morphology for x sufficiently large is illustrated below by characteristic TEM pictures for $x = 0.96$ and $x = 0.70$ (Figure 1). In the latter case the room temperature TEM is shown, but cryo-TEM gave the same result. Clearly, the ordering in the copolymer with the highest amount ($x = 0.96$) of 4VP is considerably better than in the copolymer with a fraction 0.70 of 4VP groups. The long period as it follows from these TEM pictures is ~ 4.5 nm (confirmed by image FFT). This is significantly larger than concluded from the SAXS data presented below, probably due to swelling as a result of the iodine staining. The effect of iodine staining was further studied by increasing the staining time stepwise by using 30 min intervals up to 3 h. It turns out that morphology is relatively stable up to 1.5 h staining, but longer staining will cause major swelling and will finally destroy the long-range order and sample morphology totally. In order to minimize staining artifacts, the samples were stained 20–30 min.

Polarized optical micrographs of four different $\text{P}(\text{S}_{1-x}\text{-co-4VP}_x)(\text{PDP})_{1.0}$ systems are shown in Figure 2. These demonstrate that the multidomain structure becomes finer and finer for increasing styrene fractions.

Figure 3 shows the characteristic SAXS data as a function of temperature, obtained on cooling, for five different $\text{P}(\text{S}_{1-x}\text{-co-4VP}_x)(\text{PDP})_{1.0}$ systems, with the mole fraction of 4VP varying from 1.0 to 0.568. For all but the last system, a clear order–disorder transition is observed on cooling as witnessed by a sudden strong increase in scattering together with a narrowing of the scattering peak. For $x = 1.0$, 0.965, and 0.917 the crystallization of the alkyl side chains on cooling occurs around 20°C as manifested by a sudden drop in intensity (cf. ref 15).

Figure 4 shows that the order–disorder temperatures as a function of x as determined from these SAXS data obtained on cooling with $5^\circ\text{C}/\text{min}$ decreases linearly as a function of the fraction of styrene in the random copolymer. This is a clear manifestation of the role played by styrene in relation to the interaction energy difference between the homogeneously mixed disordered state and the ordered state. To a good approximation the number of hydrogen bonds is not affected by the order–disorder transition.^{18,27} Hence, in the homogeneously mixed state, on the one hand, and the microphase-separated lamellar system state, on the other, this number is approximately the same. The essential observation is that the presence of PDP reduces the number of highly unfavorable styrene/4-vinylpyridine interactions in the *disordered* state: the so-called copolymer repulsion effect.^{4–6} In practice, this reduction will be the result of the alkyl groups of PDP being present in between some of the styrene and 4-vinylpyridine units. This will no longer be the case in the ordered lamellar state. In the range of copolymer compositions investigated, the copolymer effect will be larger for the complexes involving larger fractions of styrene. As a consequence, lower temperatures can be tolerated before microphase separation sets in. Hence, T_{ODT} will be an increasing

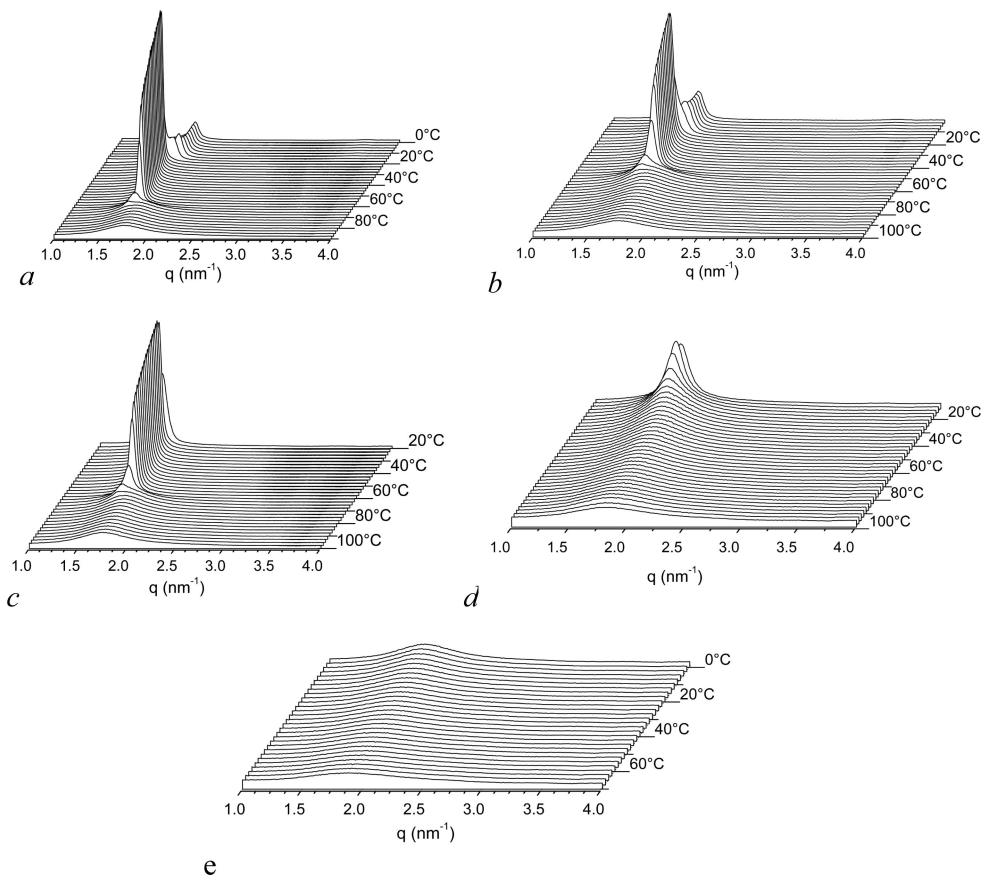


Figure 3. SAXS data as a function of temperature, obtained during cooling with a rate of 5 °C/min, for hydrogen-bonded complexes $P(S_{1-x}\text{-co-}4VP_x)(PDP)_{1.0}$ for fractions of 4VP equal to (a) 100%, (b) 96.5%, (c) 91.7%, (d) 70.3%, and (e) 56.8%.

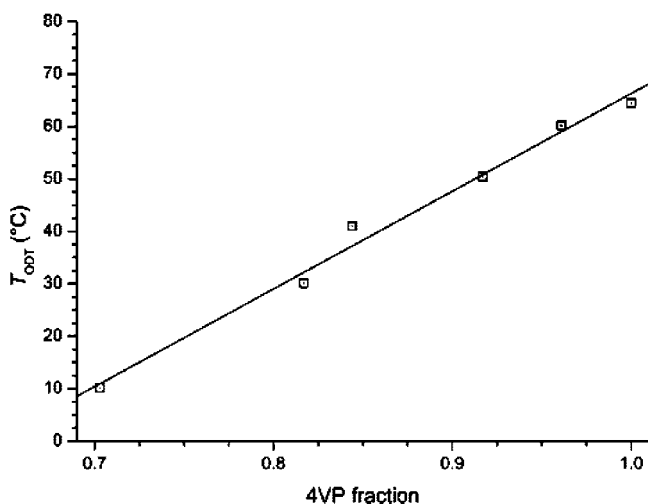


Figure 4. Order-disorder temperature, T_{ODT} , of hydrogen-bonded complexes $P(S_{1-x}\text{-co-}4VP_x)(PDP)_{1.0}$ as a function of the fraction of 4VP in the copolymer.

function of x , as observed experimentally (Figure 4). For $x = 0.7$ the ODT during cooling with 5 °C/min is around 10 °C. Since room temperature TEM shows that the lamellar structure is still present at room temperature, all ODT's determined in this manner clearly involve some supercooling.

Another interesting issue concerns the periodic spacing $d = 2\pi/q^*$, where q^* is the scattering vector value at the intensity peak position corresponding to the ordered state or the disordered state when only a correlation hole peak is observed. Figure 5 shows the values of this quantity as a function of the fraction of 4VP of the copolymer. The characteristic length scale of the

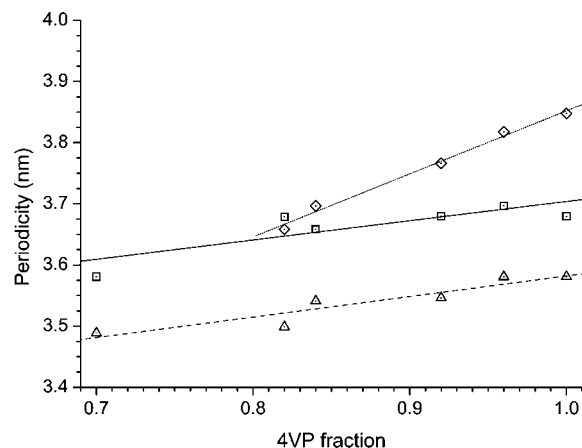


Figure 5. Periodicity of poly($S_{1-x}\text{-co-}4VP_x$)(PDP) $_{1.0}$ samples as a function of the fraction of 4VP in the copolymer: (\square) 5 °C below T_{ODT} ; (\diamond) at 30 °C, below ODT; (\triangle) at 70 °C above ODT, corresponding to the correlation hole peak.

dominant concentration fluctuations in the disordered state at a fixed temperature of 70 °C is found to be a monotonously increasing function of the 4VP fraction. The same trend is found for the periodic length scale in the ordered state both determined 5 °C below the actual T_{ODT} , and hence at different temperatures for different systems, and determined at a fixed temperature of 30 °C. In the latter case measurements are only possible for the samples with a 4VP fraction above 82%. For lower 4VP fractions the system is still in the disordered state at 30 °C.

When the complexes are in the ordered state, the observed d -spacing corresponds to a lamellar periodicity: one lamellar layer contains the polymer chains together with the hydrogen-

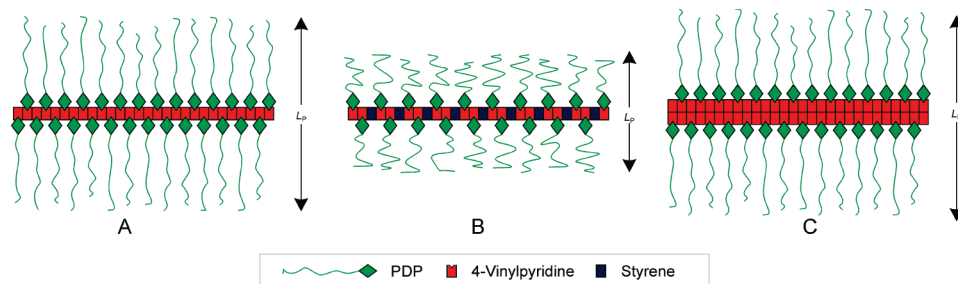


Figure 6. Schematic and strongly simplified illustration of the self-assembled state of (A) P4VP(PDP)_{1.0} compared to (B) P(S_{1-x}-co-4VP_x)(PDP)_{1.0} for $x = 0.67$ and (C) P4VP(PDP)_x for $x = 0.5$.

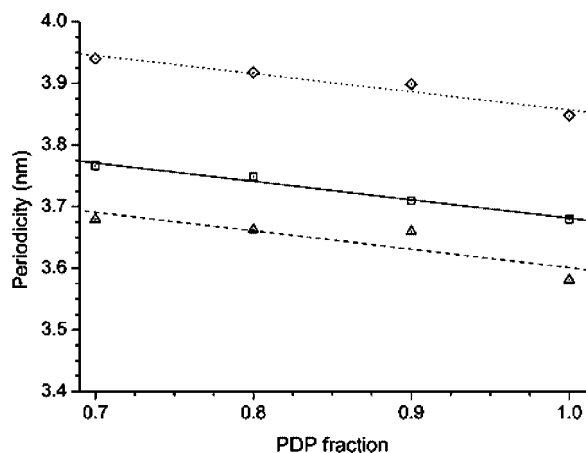


Figure 7. Periodicity of P4VP(PDP)_x samples as a function of the fraction PDP: (□) 5 °C below T_{ODT} ; (◇) below ODT at 30 °C; (Δ) above ODT at 70 °C, corresponding to the correlation hole peak.

bonded phenol groups, and the other layer is formed by the alkyl tails of PDP. The alkyl tails from adjacent layers form an interdigitating one-layer structure rather than an end-to-end double-layer structure.²⁸ The fact that the long period decreases for an increasing fraction of styrene units implies that the thickness of either of the two or both layers has to decrease. For the ordered state of pure P4VP(PDP)_{1.0}, the polymer layer is close to a monolayer since a majority of the pyridine groups are hydrogen-bonded to PDP molecules (Figure 6a).^{18,27} An obvious explanation for the long period behavior observed is that the ordered state of P(S_{1-x}-co-4VP_x)(PDP)_{1.0} still consists of a polymer monolayer now containing both styrene and 4-vinylpyridine units (Figure 6b). The PDP molecules are attached to the pyridine groups, and hence the “grafting” density of the PDP molecules will be lower for larger styrene fractions with concurrent relaxation into a more coil-like state of the alkyl tails. Of course, it may also promote further interdigitation of the alkyl tails from adjacent layers.

The data presented demonstrate that the decrease in long period going from P4VP(PDP)_{1.0} to P(S_{0.18}-co-4VP_{0.82})(PDP)_{1.0} at 30 °C is about 0.2 nm, decreasing from 3.85 to 3.65 nm. An estimation taking the model presented in Figure 6 literally results in a decrease that is only slightly larger despite the fact that the figure is in many respects an oversimplification. For the P(S_{0.18}-co-4VP_{0.82})(PDP)_{1.0} system, for instance, T_{ODT} is just above 30 °C, and strong segregation, as suggested by the illustration, is out of the question.

In P(S_{1-x}-co-4VP_x)(PDP)_{1.0} the number of PDP molecules equals the number of 4-vinylpyridine groups. If the styrene units are formally replaced by 4-vinylpyridine units without increasing the number of PDP molecules, we get the P4VP(PDP)_x system, where only a fraction x of the 4-vinylpyridine units can potentially carry a hydrogen-bonded side chain at the same time. Strikingly, the behavior of the long period of the ordered

structure of both systems, P(S_{1-x}-co-4VP_x)(PDP)_{1.0} and P4VP(PDP)_x, as a function of x turns out to be exactly opposite. Figure 7 presents the long period of P4VP(PDP)_x as a function of x and shows a monotonously decrease, where a monotonously increase was found for P(S_{1-x}-co-4VP_x)(PDP)_{1.0} (Figure 5).

This can only be explained if we assume that the thickness of the P4VP containing layer decreases as a function of x (increasing fraction PDP), whereas the stretching of the alkyl tails remains practically the same. The 4VP groups that do not carry a hydrogen-bonded side chain apparently are buried inside the P4VP layers unlike the styrene units in the P(S_{1-x}-co-4VP_x)(PDP)_{1.0} systems (Figure 6c).

Conclusions

We addressed the effect of styrene monomer units on the lamellar self-assembly of hydrogen-bonded complexes of random copolymers of styrene and 4-vinylpyridine, P(S_{1-x}-co-4VP_x), with pentadecylphenol (PDP). Taking one PDP molecule per 4-pyridine unit, we observed a decrease in both the order–disorder transition temperature (ODT) and the periodic length scale for increasing fractions of styrene. The decrease in ODT is argued to be due to the screening of the highly unfavorable styrene–pyridine interactions by the alkyl units in the isotropic melt state. The decrease in long period shows that the alkyl tails adopt a more coil-like conformation in the presence of styrene units. In contrast, the periodicity of lamellar P4VP(PDP)_x, where also only a fraction x of the total number of monomers of the macromolecule may potentially hydrogen bond with PDP molecules at the same time, increases for decreasing amounts of PDP. Here the alkyl tails do not adopt a more coil-like conformation but remain strongly stretched like in the stoichiometric P4VP(PDP)_{1.0} complex. The free 4-vinylpyridine units avoid the alkyl layer and are simply buried inside the 4-vinylpyridine layer.

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