

# Intermediate Segregation Type Chain Length Dependence of the Long Period of Lamellar Microdomain Structures of Supramolecular Comb–Coil Diblocks

E. Polushkin,<sup>†</sup> G. O. R. Alberda van Ekenstein,<sup>†</sup> M. Knaapila,<sup>‡</sup> J. Ruokolainen,<sup>‡</sup> M. Torkkeli,<sup>§</sup> R. Serimaa,<sup>§</sup> W. Bras,<sup>⊥</sup> I. Dolbnya,<sup>⊥</sup> O. Ikkala,<sup>\*,‡</sup> and G. ten Brinke<sup>\*,†,‡</sup>

Dutch Polymer Institute, Laboratory of Polymer Chemistry, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands; Department of Engineering Physics and Mathematics, Materials Physics Laboratory, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo Finland; Department of Physics, University of Helsinki, P.O. Box 9, FIN-00014, Helsinki, Finland; and Netherlands Organization for Scientific Research (NWO) DUBBLE CRG/ESRF, c/o BP 220, Grenoble F38043, France

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**ABSTRACT:** A characteristic intermediate segregation type chain length dependence of the long period  $D$  of the lamellar microdomain structure of a class of comb–coil supramolecules is reported. The supramolecular comb–coil diblock copolymers studied consist of a polystyrene (PS) “coil” block and a “comb” block of poly(4-vinylpyridine) (P4VP) either hydrogen bonded to pentadecyl phenol (PDP) (i.e., P4VP(PDP)-*b*-PS) or first protonated with methanesulfonic acid (MSA) and then hydrogen bonded to PDP (i.e., P4VP(MSA)(PDP)-*b*-PS). In both cases we find a scaling  $D \sim N_{\text{tot}}^{\delta}$ ,  $\delta \cong 0.8$ , where  $N_{\text{tot}}$  denotes the total number of monomers of the P4VP-*b*-PS backbone. In the case of diblock copolymers this would correspond to a characteristic intermediate segregation regime behavior. Pure PS-*b*-P4VP, on the other hand, shows the expected strong segregation behavior  $D \sim N_{\text{tot}}^{\delta}$ ,  $\delta \cong 0.7$ .

## 1. Introduction

During the past decade, considerable progress has been made in our understanding of the melt phase behavior of block copolymers. The first comprehensive analysis of microphase separation in diblock copolymer systems was made by Leibler.<sup>1</sup> Using a Landau free energy expansion, the phase diagram was calculated in the so-called weak segregation limit (WSL) characterized by a spatially slowly varying composition profile. The opposite strong segregation limit (SSL), characterized by sharp interface boundaries, was considered in some detail by Semenov.<sup>2</sup> Using a full self-consistent field theory, developed by Matsen and Schick<sup>3</sup> and based on earlier work by Helfand and co-workers,<sup>4,5</sup> Matsen and Bates were able to unify the weak and strong segregation theories.<sup>6</sup>

In this paper we focus on the functional dependence of the long period  $D$  of the lamellar microdomain structures on the chain length  $N$ . This functional dependence is strongly dependent on the position in the phase diagram. The assumption that the chain conformations are close to Gaussian ( $D \sim N^{1/2}$ ) underlies the use of the random phase approximation in conjunction with the Landau free energy expansion.<sup>1,7</sup> Experiments indicate, however, that the conformation of the polymer chains starts to deviate strongly from the homogeneous melt situation on approaching the order–disorder transition (ODT).<sup>8–11</sup> The chains are severely stretched, and the position of the correlation hole peak ( $2\pi/q^*$ ) in the disordered melt and the long period  $D$  of the lamellar microdomain structure in the ordered melt both scale as  $N^{0.8}$ . This scaling behavior remains valid throughout

the intermediate segregation regime. “Anomalous” exponent values for diblock copolymers in the intermediate segregation regime were anticipated in several theoretical papers.<sup>6,12,13</sup> Still deeper inside the phase diagram, the interfaces between the domains become really sharp and the SSL is reached, where  $D \sim N^{0.67, 2.6, 11–14}$

The mean-field prediction for the transition temperature, ignoring fluctuation corrections, is  $\chi N \cong 10.5$ , where  $\chi$  denotes the Flory–Huggins interaction parameter. The transition from the Gaussian conformation to the stretched conformation occurs around  $\chi N \cong 5–6$ , whereas the subsequent transition to the strong segregation regime characterized by the 0.67 scaling law occurs at  $\chi N \cong 30–100$ .<sup>9–11</sup>

During recent years our efforts have concentrated on the synthesis of self-organized functional materials using a combination of supramolecular principles and block copolymers.<sup>15–22</sup> One class of systems studied extensively consists of comb–coil supramolecules prepared by using diblock copolymers of poly(4-vinylpyridine) and polystyrene (P4VP-*b*-PS) with side chain amphiphiles such as pentadecylphenol (PDP) hydrogen bonded to the P4VP-block. Below ca. 70 °C, these P4VP-(PDP)-*b*-PS comb–coil supramolecules self-organize in the form of *structure-within-structure* morphologies, with a large length scale structure due to the separation between the comb- and coil-block and a short length scale lamellar structure due to additional microphase separation inside the comb-block domains.<sup>15,16</sup> The thermoreversibility of the side chain bonding can be used to prepare mesoporous materials consisting of a PS matrix with hexagonal arranged hollow cylinders with short P4VP brushes at the interior wall.<sup>19</sup> The opposite case of “crew-cut” cylindrical aggregates consisting of a PS core and a thin corona of short P4VP chains has also been realized.<sup>20</sup> In a slightly more complicated example, P4VP is first protonated with a

<sup>†</sup> University of Groningen.

<sup>‡</sup> Helsinki University of Technology.

<sup>§</sup> University of Helsinki.

<sup>⊥</sup> Netherlands Organization for Scientific Research.

**Table 1. Characteristics of P4VP-*b*-PS Diblock Copolymers**

sample	P4VP (g/mol)	PS (g/mol)	$M_w/M_n$	$N_{tot}$	P4VP weight fraction
P1037	4 750	3 300	1.07	77	0.59
P779	11 770	8 700	1.09	196	0.57
P105	20 700	21 400	1.13	403	0.49
P111	29 400	19 900	1.15	471	0.60
P234	43 500	56 300	1.20	956	0.44

strong acid such as methanesulfonic acid (MSA) to which subsequently PDP is hydrogen bonded, leading to P4VP(MSA)(PDP)-*b*-PS. The presence of MSA increases the ODT of the short length scale structure to 100 °C. Below this temperature similar *structure-within-structure* morphologies are found as in the previous case of supramolecules without MSA. Because P4VP(MSA) is a conducting salt, the various transitions observed in this system as a function of temperature are directly reflected in the conductivity.<sup>17</sup>

Here, we are interested in the behavior of the long period of the large length scale lamellar microdomain structures of both P4VP(PDP)-*b*-PS and P4VP(MSA)(PDP)-*b*-PS as a function of the molecular weight of the backbone, i.e., the parent P4VP-*b*-PS diblock copolymer. Our interest is derived from the observation that the presence of a great many side chains could lead to strong stretching of the P4VP backbone. The conformational properties of comb copolymers in a dilute solution of a good solvent has been the subject of many studies involving theoretical modeling,<sup>23–26</sup> computer simulations,<sup>27–30</sup> and experiments.<sup>31,32</sup> There is ample evidence that the steric interactions between the side chains may result in a stiff cylindrical comb copolymer brush structure. Of course, the melt state considered here is considerably different due to the screening of the excluded-volume effect.<sup>7</sup> Furthermore, the side chains are not covalently bonded but rather linked by hydrogen bonds. Still, there is some evidence suggesting that, in the comb-coil supramolecules studied here, the presence of the side chains gives rise to additional stretching. On increasing the temperature a very strong decrease in long period of P4VP(PDP)-*b*-PS and P4VP(MSA)(PDP)-*b*-PS was observed, much stronger than for pure P4VP-*b*-PS diblock copolymers.<sup>33</sup> Of course, this could also simply be due to an increase in free PDP acting as a diluent.<sup>34</sup>

## 2. Experimental Section

**Materials.** Three series of samples were used. Five diblock copolymers of poly(4-vinylpyridine) and polystyrene (P4VP-*b*-PS) were used for the determination of the chain length dependence of the long period of the pure diblock copolymers; see Table 1 for block lengths and polydispersities. A different series of 10 P4VP-*b*-PS diblock copolymers were used for the preparation of the comb-coil supramolecules P4VP(PDP)<sub>1.0</sub>-*b*-PS and P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS. The first class of comb-coil supramolecules consists of P4VP-*b*-PS with a stoichiometrical amount (with respect to the number of pyridine groups) of pentadecylphenol (PDP) hydrogen bonded to the P4VP block. In the last class, the P4VP block is first stoichiometrically protonated with methanesulfonic acid (MSA) and subsequently hydrogen bonded with a stoichiometric amount of PDP. Scheme 1 shows the expected bonding. The characteristics of these PS-*b*-P4VP diblock copolymers as well as the P4VP(PDP)<sub>1.0</sub>-*b*-PS and P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS supramolecules are given in Table 2.  $N_{tot}$  refers to the total number of monomers (styrene + 4-vinylpyridine) of the PS-*b*-P4VP diblock copolymer. All diblock copolymers were obtained from Polymer Source, Inc., and used as received. PDP was pur-

chased from Pfalz&Bauer (purity 97%). Before use, it was recrystallized from petrol ether at −20 °C and then dried in a vacuum at 60 °C for 24 h. MSA was obtained from Merck-Schuchardt and used without further purification.

**Sample Preparation.** The P4VP(PDP)<sub>1.0</sub>-*b*-PS complexes were prepared by dissolving P4VP-*b*-PS and PDP in analysis-grade chloroform. The concentration of polymer in the solvent was kept low to ensure homogeneous complex formation. The solutions were then dried in air, and the final drying was performed at 55 °C in a vacuum for ca. 2 days. The material was stored in a desiccator.

In the case of the P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS complex, first a specific amount of P4VP-*b*-PS copolymer was dissolved in a 1% w/w solution of MSA in chloroform to obtain nominally one pyridine group for each MSA molecule. Then the PDP was added again to obtain nominally one PDP molecule per pyridine (and MSA) group. The drying procedure was the same as for P4VP(PDP)<sub>1.0</sub>-*b*-PS.

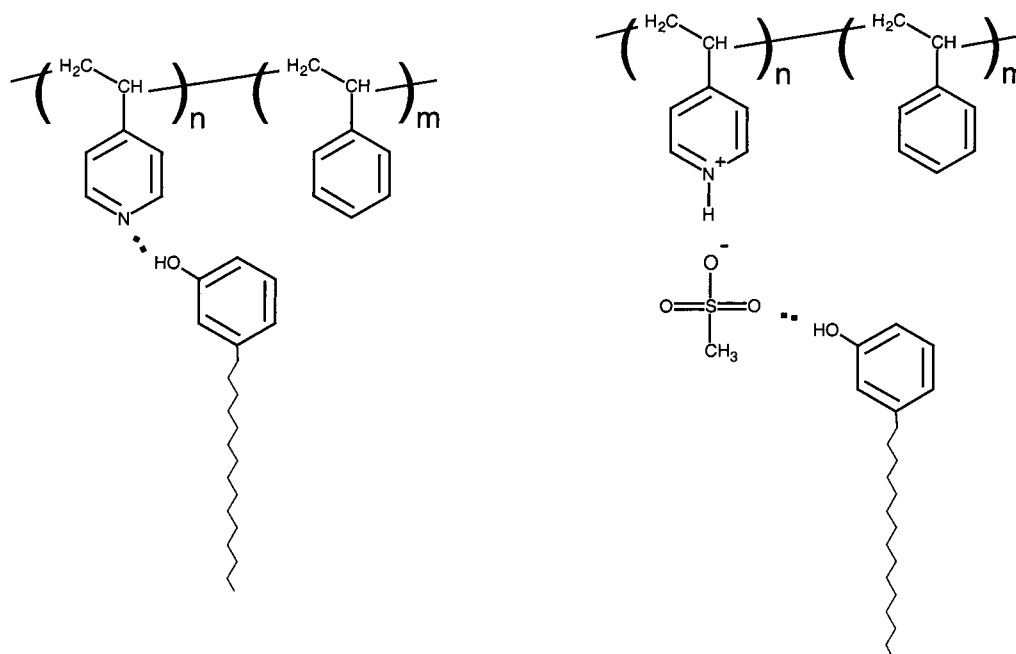
**Small-Angle X-ray Scattering.** SAXS measurements were performed using an in house NanoStar device (Bruker-AXS and Anton Paar) and at the European Synchrotron Radiation Facility (ESRF, beam line BM26 “DUBBLE”) in Grenoble. In the case of the NanoStar a ceramic fine-focus X-ray tube has been used in a point focus mode. The tube is powered with a Kristalloflex K760 generator at 35 kV and 40 mA. The primary beam is collimated with cross-coupled Göbel mirrors and a pinhole of 0.1 mm in diameter providing a Cu K $\alpha$  radiation beam ( $\lambda = 0.154$  nm) with a full width at half-maximum about 0.2 mm at the sample position. The sample-detector distance was varied from 0.64 to 1.08 m. Using a Hi-Star position-sensitive area detector (Siemens-AXS) allowed recording the scattering intensity in the  $q$  range 0.08–3 nm<sup>−1</sup>. The scattering vector  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\lambda$  is the wavelength and  $\theta$  the scattering angle. The data presented in Figure 1 have been taken with the NanoStar device, collecting the data for 15 min at different temperatures. In the case of the ESRF experiments,  $\lambda = 0.103$  nm ( $E = 12$  keV) and a beam size of approximately 1 mm<sup>2</sup> were chosen for the measurements. The sample-detector distance was 7.5 m. A two-dimensional detector was used to measure the intensity of a scattering cone quarter at a  $q$  range of 0.06–1.2 nm<sup>−1</sup>. The scattering data reported in Figures 3 and 5 were measured during heating with 10 °C/min collecting the data during 30 s for each frame.

**Shearing.** To obtain more pronounced SAXS patterns, some of the comb-coil supramolecular samples were first oriented by shearing in an oscillation mode. The procedure was performed with a Rheolyst AR1000 rheometer (TA Instrument) at 1 Hz and a shear strain of 50%. The duration of the shearing was ca. 30 min. The shearing temperature was varied from 115 to 140 °C, depending on the molecular characteristics of the parent P4VP-*b*-PS copolymers. More details about the shear procedure and the demonstration that such a procedure leads to a more perfect macroscopic orientation in the case of these supramolecules can be found in ref 35.

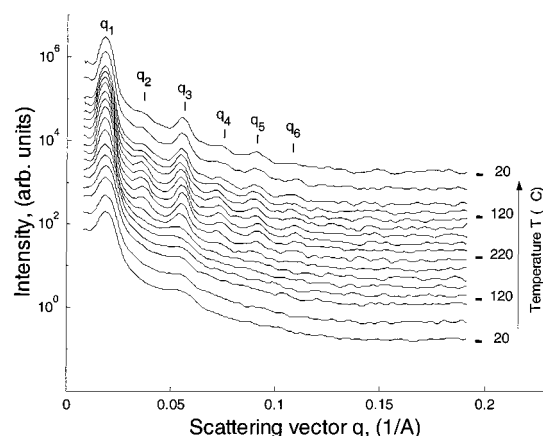
## 3. Results and Discussion

The value of the Flory–Huggins  $\chi$ -parameter between polystyrene (PS) and poly(4-vinylpyridine) (P4VP) has been a subject of debate lately.<sup>36–38</sup> A comprehensive study, based on the phase behavior in blends of polystyrene and *random* copolymers of styrene and 4-vinylpyridine, indicated that  $\chi \approx 0.34$  (taking the styrene monomer as segment) at ca. 160 °C.<sup>37</sup> In the two other studies<sup>36,38</sup> no precise values are given. However, the authors in ref 36 concluded on the basis of their results 0.38 to be a lower bound while the actual value is probably much larger. The authors of ref 38 even concluded that  $\chi > 2.3$  at 70 °C. At any rate, for molecular weights of ca. 10 000 and higher, the P4VP-*b*-PS system should be in the strong segregation regime where the molecular weight scaling of the long period is characterized by a 0.67 scaling exponent.<sup>2</sup> To verify

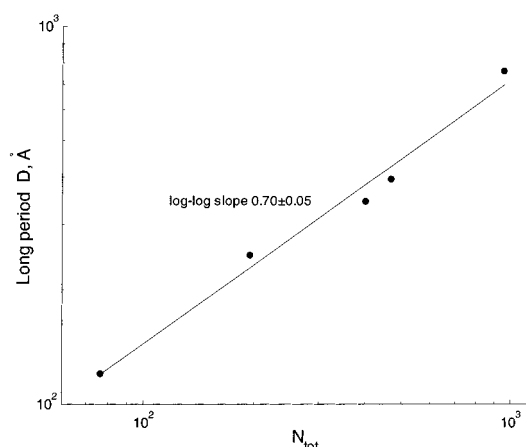
Scheme 1

Table 2. Characteristics of P4VP(PDP)<sub>1.0</sub>-*b*-PS and P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS Comb-Coil Supramolecules

sample	P4VP (g/mol)	PS (g/mol)	$M_w/M_n$	$N_{tot}$	P4VP weight fraction	P4VP(PDP) <sub>1.0</sub> weight fraction	P4VP(MSA) <sub>1.0</sub> (PDP) <sub>1.0</sub> weight fraction
P103	5 100	19 600	1.08	237	0.21	0.50	0.56
P99	8 080	32 900	1.05	393	0.20	0.49	0.54
P136	13 200	31 900	1.08	432	0.29	0.62	0.67
P138	5 600	40 000	1.09	438	0.12	0.35	0.41
P110	20 900	47 600	1.14	657	0.31	0.63	0.68
P227	24 700	57 300	1.14	786	0.30	0.63	0.68
P251	30 200	71 900	1.13	979	0.30	0.62	0.67
P232	30 300	78 900	1.22	1047	0.28	0.60	0.65
P252	32 700	92 700	1.13	1203	0.26	0.58	0.63
P235	33 500	128 400	1.17	1554	0.21	0.50	0.56

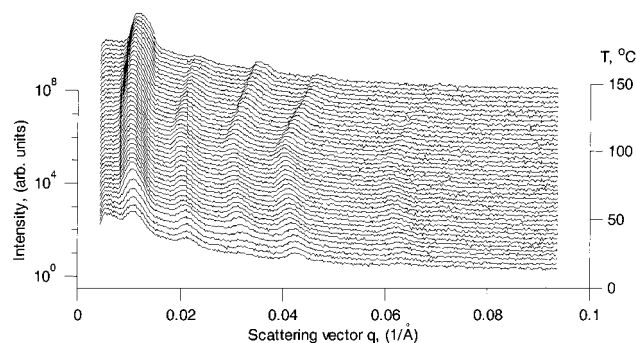
Figure 1. Small-angle X-ray patterns of the P4VP(20.7K)-*b*-PS(21.4K) diblock copolymer (P105, Table 1) as a function of temperature (NanoStar).

this, a number of P4VP-*b*-PS diblock copolymers (see Table 1) exhibiting lamellar microphase-separated morphologies were investigated by small-angle X-ray scattering (SAXS). Figure 1 shows a series of SAXS pattern for the P4VP(20.7K)-*b*-PS(21.4K) block copolymer (P105, cf. Table 1) as a function of temperature during heating and cooling. The positions of the lamellar peaks are only weakly dependent on temperature in the temperature range (20–220 °C) investigated. Figure 2 presents in a log–log plot the long period  $D$  of the lamellar structure

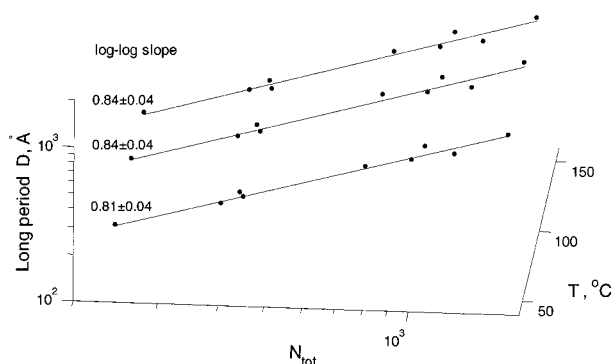
Figure 2. A log–log plot of the long period  $D$  of a series of P4VP-*b*-PS diblock copolymers listed in Table 1 at 30 °C, as a function of the total number of monomers  $N_{tot}$  of the diblock copolymers. The actual data are in Table 3.

at 30 °C for this series of P4VP-*b*-PS diblock copolymers as a function of the block copolymer chain length. The latter is approximated by the total number of monomers of the diblock copolymer,  $N_{tot}$ . The actual data are listed in Table 3. A linear least-squares fit to the data gives a value of  $0.70 \pm 0.05$  for the chain length scaling exponent ( $D \sim N_{tot}^{0.7}$ ), close to the theoretical strong segregation value of 0.67.

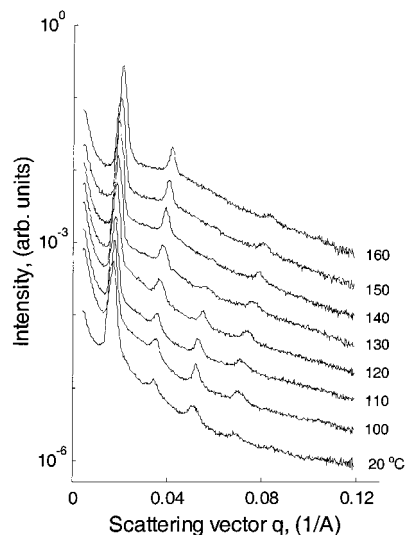




**Figure 3.** Small-angle X-ray patterns of the P4VP(30.2K)-(PDP)<sub>1.0</sub>-b-PS(71.9K) comb-coil supramolecule (P251, Table 2) as a function of temperature during heating with 10 °C/min (ESRF).



**Figure 4.** A log-log plot of the long period  $D$  of a series of P4VP(PDP)<sub>1.0</sub>-b-PS comb-coil supramolecules listed in Table 2 at 60, 110, and 150 °C as a function of the total number of monomers  $N_{\text{tot}}$  of the P4VP-b-PS diblock copolymers. The actual data are in Table 4.



**Figure 5.** Small-angle X-ray patterns of the P4VP(13.2K)-(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-b-PS(31.9K) comb-coil supramolecule (P136, Table 2) as a function of temperature during heating with 10 °C/min (ESRF).

Before we consider the P4VP(PDP)-b-PS and P4VP-(MSA)(PDP)-b-PS comb-coil supramolecules, let us first present a simple strong segregation argument for the case of comb-coil diblock copolymers. We will consider the most simple case of a P(A) block of  $N_A$  segments and a comb block consisting of a P(B) backbone of  $N_B$  segments grafted with chemically identical side chains of  $M$  segments. All segments have equal size  $a^3$ . The free energy of a lamellar structure is then given by

**Table 3. Long Period of P4VP-b-PS at 30 °C**

sample	$N_{\text{tot}}$	Lp [nm]	sample	$N_{\text{tot}}$	Lp [nm]
P1037	77	12.0	P111	471	39.2
P779	196	24.6	P234	956	75.7
P105	403	34.3			

(ignoring all irrelevant numerical factors)

$$F/kT \cong \gamma\sigma + h_A^2/N_A a^2 + h_B^2/N_B a^2 \quad (1)$$

Here  $\gamma \sim \chi^{1/2}$  is the interfacial tension, where  $\chi$  is the Flory-Huggins interaction parameter between the A and B segments,  $\sigma$  is the area per chain, and  $h_A$  and  $h_B$  are the extensions of the P(A) and P(B) backbone blocks, respectively. We assume that the side chains satisfy unperturbed Gaussian statistics due to the screening of the excluded-volume effect. Minimization of eq 1 using the self-consistent conditions

$$h_A \sigma = N_A a^3 \quad (2a)$$

$$h_B \sigma = (N_B + N_B f M) a^3 \quad (2b)$$

where  $fN_B$  is the number of side chains, leads to

$$h_A \cong \chi^{1/6} \frac{N_A}{(N_A + N_B(1 + fM))^{1/3}} a \quad (3a)$$

$$h_B \cong \chi^{1/6} \frac{N_B(1 + fM)}{(N_A + N_B(1 + fM))^{1/3}} a \quad (3b)$$

Hence

$$D = h_A + h_B \cong \chi^{1/6} \frac{N_A + N_B(1 + fM)}{(N_A + N_B(1 + fM))^{1/3}} a \quad (4)$$

This expression is considerably more complicated than for the pure diblock copolymer case (corresponding to  $f = 0$ ). To obtain a lamellar structure,  $N_A$  and  $N_B(1 + fM)$  should have similar values. Assuming  $N_A \cong N_B(1 + fM)$ , we find  $D \sim (N_A + N_B(1 + fM))^{2/3}$ . In other words, in that particular case the same chain length dependence as in the case of diblock copolymers is found provided the chain length is taken to be the total length, i.e., backbone plus side chains.

The actual situation at hand is considerably more complicated. Even the simplest description will require at least three different  $\chi$ -parameters. Moreover, the side chains are attached by hydrogen bonds, and hence, some free amphiphiles will be present as well. Furthermore, the interface will be enriched by the amphiphiles (free or bonded) given the strongly unfavorable PS/P4VP interaction. In addition, for the systems studied, the weight fractions of the supramolecular comb blocks vary from 0.35 to 0.63 in the case of P4VP(PDP)-b-PS and from 0.41 to 0.68 in the case of P4VP(MSA)(PDP)-b-PS (cf. Table 2). Since the weight fraction corresponds roughly to the volume fraction, the above-mentioned condition  $N_A \cong N_B(1 + fM)$  is also not generally valid for our limited number of samples. Hence, it is not that clear which parameter is most appropriate to express the functional dependence of the long period of our comb-coil supramolecules. We therefore decided to

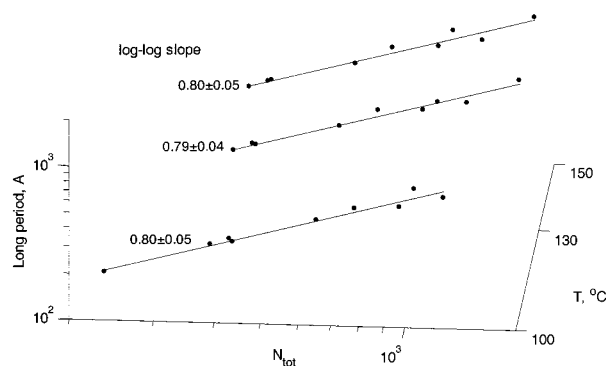
**Table 4. Long Period of P4VP(PDP)<sub>1.0</sub>-*b*-PS at Various Temperatures**

sample	no. of monomers of P4VP- <i>b</i> -PS $N_{\text{tot}}$	Lp [nm]		
		60 °C	110 °C	150 °C
P103	237	20.1	18.7	17.2
P99	393	29.2	27.7	25.4
P136	432	34.7	32.7	29.2
P138	438	32.7	30.0	26.0
P227	786	54.7	54.6	48.3
P251	979	61.5	58.1	52.3
P232	1047	76.6	73.0	66.1
P252	1203	68.0	63.4	58.1
P235	1554	93.7	93.7	86.0

present the long period of these systems as a function of the length of the parent P4VP-*b*-PS diblock copolymer.

We consider first the series of P4VP(PDP)-*b*-PS comb-coil supramolecules (Table 2), obtained by combining P4VP-*b*-PS diblock copolymers with a stoichiometric (with respect to the number of hydrogen bonds) amount of PDP. From previous FTIR studies<sup>16</sup> it is known that the degree of hydrogen bonding is large as long as the temperature is not too high. The relative lengths of the P4VP- and PS-block have been chosen in such a way that the resulting comb weight fraction is between 0.35 and 0.63, leading to a lamellar microdomain structure of alternating PS and P4VP(PDP) layers. As is well-known now, below ca. 70 °C, an additional lamellar ordering with a long period of ca. 3.5 nm takes place in the P4VP(PDP) domains. In this way a two-length-scale *lamellar-within-lamellar* morphology is formed.<sup>15,17</sup> Figure 3 presents the SAXS patterns of the sample based on the parent P4VP-(30.2K)-*b*-PS(71.9K) diblock copolymer at various temperatures, illustrating the large length scale lamellar structure. The short length scale structure and the corresponding order-disorder transition can only be seen at larger angles (cf. ref 39).

We are mainly interested in the effect of the comb-shape character of the P4VP(PDP) block on the long period. Since the hydrogen bonding is so temperature sensitive, we restrict the analysis to temperatures not exceeding 150 °C. The glass transition temperature of P4VP ( $T_g \approx 150$  °C) is strongly depressed due to the presence of PDP. The P4VP(PDP) layers are still in the melt state at temperatures as low as 30 °C,<sup>40</sup> whereas the PS layers are in the glassy state below ca. 90 °C. The order-disorder transition inside the P4VP(PDP) layers occurs around 70 °C. On the basis of these considerations, we determined the long period  $D$  of a series of lamellar P4VP(PDP)-*b*-PS systems at 60, 110, and 150 °C. Figure 4 presents the results, listed in Table 4, as a function of the number of monomers  $N_{\text{tot}}$  of the backbone. The solid lines represent the linear fits in the range  $N_{\text{tot}} = 237$ –1554. Surprisingly, the exponent values turn out to be  $0.81 \pm 0.04$ ,  $0.83 \pm 0.04$ , and  $0.84 \pm 0.04$ . This is very similar to the intermediate segregation regime values reported by Hadzioannou and Skoulios<sup>8</sup> for diblock and triblock copolymers of styrene and isoprene, by Almdal et al.<sup>9</sup> for poly(ethylene-propylene)-*b*-poly(ethylene) diblock copolymers, and by Papadakis et al.<sup>10</sup> for polystyrene-*b*-polybutadiene diblock copolymers. Of course, it does not automatically follow that the P4VP(PDP)-*b*-PS systems studied also fall within the intermediate segregation regime. The simple theoretical analysis presented above already indicated that the number of backbone monomers is not

**Figure 6.** A log-log plot of the long period  $D$  of a series of P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS comb-coil supramolecules listed in Table 2 at 100, 130, and 150 °C as a function of the total number of monomers  $N_{\text{tot}}$  of the P4VP-*b*-PS diblock copolymers. The actual data are in Table 5.

necessarily the most appropriate parameter. Still, it could be an indication that these systems are really in the intermediate segregation regime. In the previous section we considered the P4VP-*b*-PS block copolymers and concluded that those systems were in the strong segregation regime, which came as no surprise in view of the large value of the interaction parameter. For P4VP(PDP)-*b*-PS, however, the interface will be enriched by the alkyl tails of the amphiphiles and/or by some free PDP, thereby reducing the interfacial tension considerably. In this respect, it is of interest to mention the miscibility of PDP and PS above ca. 135 °C. That the interface enrichment by the alkyl tails of the side chains may be real has already been shown in a recent preliminary self-consistent-field study.<sup>41</sup> Moreover, the fact that the exponent value is also  $0.84 \pm 0.04$  at 150 °C, where many of the hydrogen bonds are already broken and part of the PDP has diffused into the PS layers, corroborates the conclusion that these systems actually are in the intermediate segregation regime.

Next we turn our attention to the P4VP(MSA)(PDP)-*b*-PS systems. Figure 5 presents the SAXS patterns of the sample based on the parent P4VP(13.2K)-*b*-PS(31.9K) diblock copolymer at different temperatures. In this case the weight fraction of the comblike material is ca. 67%. As demonstrated by the SAXS data, the system has a lamellar microdomain structure up to 160 °C. As in the previous case, the number of hydrogen bonds decreases as a function of temperature. But, there is also a remarkable difference between the systems with and without MSA. To illustrate this, we first recall the corresponding case of homopolymer P4VP. For both P4VP(PDP) and P4VP(MSA)(PDP), the number of hydrogen bonds decreases as a function of temperature. However, in the latter system this leads to macrophase separation at ca. 175 °C.<sup>17</sup> For the block copolymer-based systems discussed here, this has as a consequence that in the MSA-based samples a much stronger driving force is present to push "free" PDP into the PS layers. For this the fact that PDP becomes miscible with PS at ca. 135 °C is of course essential. As a consequence, in P4VP(MSA)(PDP)-*b*-PS systems with a lamellar microdomain structure at low temperatures, at elevated temperatures generally an order-order transition to a cylindrical morphology with P4VP(MSA) cylinders is observed.<sup>17,33</sup> As long as we restrict ourselves to temperatures below 160 °C, however, all samples but one (P103, Table 2) maintain a lamellar morphology. Figure 6 presents the long period of P4VP(MSA)(PDP)-*b*-PS,

**Table 5. Long Period of P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS at Various Temperatures**

sample	no. of monomers of P4VP- <i>b</i> -PS $N_{\text{tot}}$	Lp [nm]		
		100 °C	130 °C	150 °C
P103	237	20.6		
P99	393	32.3	29.3	28.3
P136	432	35.7	32.9	30.9
P138	438	33.7	32.2	31.6
P110	657	48.7	43.9	41.9
P227	786	58.7	56.6	53.7
P251	979	61.0	58.1	56.1
P232	1047	79.4	67.4	70.5
P252	1203	70.6	65.4	62.1
P235	1554		95.1	88.4

listed in Table 5, as a function of the parent P4VP-*b*-PS diblock copolymer molecular weight at 100, 130, and 150 °C. The scaling exponent values of  $0.80 \pm 0.05$ ,  $0.79 \pm 0.04$ , and  $0.80 \pm 0.05$  are again the same as found in the intermediate segregation regime of linear block copolymers. As before, a possible explanation is the reduction in the interfacial tension due to the enrichment of the interface with amphiphiles (PDP).

#### 4. Conclusions

Small-angle X-ray scattering experiments show P4VP-*b*-PS diblock copolymers, with total molecular weights of 8000 and higher, to be in the strong segregation limit. This comes as no surprise considering the strongly unfavorable interaction between these two components. Comb-coil supramolecules P4VP(PDP)<sub>1.0</sub>-*b*-PS and P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>-*b*-PS, however, exhibit a chain length dependence of the long period of the lamellar structure which is the same as found for linear block copolymers in the intermediate segregation regime. This could in principle be due to the different architecture. On the other hand, the enrichment of the interface by the amphiphiles (free and/or bonded) will also lower the interfacial tension considerably, thus creating a diffuse interface corresponding to intermediate rather than strong segregation behavior.

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