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Specific Adsorption of Some Styrene/Vinylpyridine Diblocks from Selective Solvents onto Solid Substrates—An NMR Study

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ABSTRACT: Interactions of styrene-*b*-4-vinylpyridine P(S-*b*-4VP) diblocks with various particulates were investigated. Proton nuclear magnetic resonance (^{1}H NMR) was used to determine the quantities of copolymer diblocks in solution. The effects of both diblock chain length and of quantity of adsorbed diblock were investigated. It was found that surface interactions lead to preferential adsorption of the 4VP chain segments onto the particulates. Isotherms show that there is a direct correlation between the normalized equilibrium quantities of adsorbed copolymer diblocks and the length of the 4VP anchor. A linear relationship also was obtained between the equilibrium quantities per unit area of substrate and the acid/base properties of the particulates, as expressed by the ratio of acceptor number to donor number (as defined by the Gutmann theory). Using the scaling model of Marques, Joanny, and Leibler, good agreement was found between the experimental and predicted equilibrium quantities of adsorbed material. For these systems, it was demonstrated that the prefactor of the scaling law relation was directly related to the acid/base properties of the substrate, and that this prefactor could be calculated from the values of the acid/base surface indices obtained by inverse gas chromatography.

1. Introduction

The study of polymers at solid interfaces in terms of their adsorption dynamics and the resulting microstructures is important, since adsorbed polymers are now used in many commercial applications such as coatings, adhesives, and composites. The mutual interactions of the adsorbed polymer layer with the filler on the one hand, and the polymer matrix on the other, largely determine the properties of the system.

In order to refine the design of polymers for composites applications, one must characterize their interaction with a given substrate. Recently, it was shown that a number of techniques could be used to determine to what extent the polymer interacts with the substrate, e.g., NMR,[1] the surface-force techniques,[2,3] ellipsometry,[4] Raman,[5] and inverse gas chromatography (IGC).[6–9] Users of these methods were generally able, via models, to characterize the type of interphase formed and to determine the thickness of the adsorbed layer.

The use of diblock copolymers in a selective solvent presents interesting opportunities and advantages to obtain information on the interaction between the polymer and the particulate. Block copolymers belong to a category of polymers which possess inherent interfacial activity. In solution, a preferential affinity by the substrate for one of the blocks leads to the formation of an adsorbed layer in which the anchoring block forms a phase that is bound to the substrate. The nonadsorbing block, which is covalently bound to the adsorbed block, dangles in the solution.

Many adsorption regimes can be envisaged for these diblocks in selective solvents. Conveniently, an effective chemical potential (μ) can be associated with each of the regimes. At the lower end of the adsorption spectrum, the effective chemical potential is very low, which leads to systems in which no adsorption is present. As μ increases, a sequence of regimes can best describe the adsorption, i.e., Rollin, van der Waals–Buoy (VDWB), Buoy dominated, and Anchor dominated. In order for a specific system to belong to a particular regime, certain conditions must be met. Qualitatively, for the system to be in the Anchor-dominated regime, which is at the high end of the adsorption spectrum, two conditions are relevant. First, a strong interaction between the substrate and the anchor must be present. Second, the copolymer diblock anchor must be very long, while the other block must be short. These considerations can also be applied to an intermediate regime such as the VDWB. For the system to be in that regime, the anchor/substrate interaction should be weaker than in the Anchor regime and the asymmetry between the two dissimilar blocks not as large. As will be explained in the discussion section, the systems studied here are in the VDWB regime.

In the past, several theories have been proposed to describe the adsorption and conformation of polymer chains on surfaces.[10] The scaling model is particularly suitable in describing the adsorption of block copolymers from selective solvents.[11] This theoretical model, due to Marques, Joanny, and Leibler (MJL), pertains to the adsorption of A–B diblock copolymers onto a solid plane in a highly selective solvent. The A part is in a poor solvent (e.g., poly-VP in toluene) and forms a "molten" layer on the solid wall of the particulate where the solvent does not penetrate. The B part is in a good solvent (e.g., polystyrene in toluene), and forms a brush grafted onto the molten layer. The structure of the adsorbed film is governed by the chemical potential of the solution in contact with the wall. The authors present a scaling theory of micelle and lamella formation as a function of the geometry of the adsorbed film. For single chains in solution, the well-solvated block (B) is assumed to take the configuration of a swollen coil, while the poorly solvated block (A) is in the

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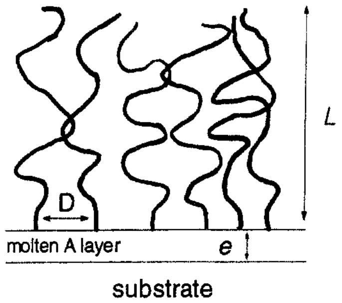

Figure 1. Illustration of the parameters of the MJL model, where L, e and D are, respectively, the equilibrium average brush height, the thickness of the film, and the average distance between the copolymer junction point.

form of a collapsed globule (blob) plasticized by the solvent. This A block, upon adsorption, forms a thin concentrated film that wets the substrate surface completely. The radius of gyration of the dissimilar segments can be expressed by

$$R_A = a_A N_A^{1/2} \qquad R_B = a_B N_B^{3/5}$$

where a is the monomer length (a_A = 2.5 Å and a_B = 1.9 Å[12]), R_A and R_B are the radii of gyration of the A and B blocks, respectively, and N_A and N_B are their respective numbers of units.

In this model, the surface density (σ) and the thickness of the film (e) are interrelated. They can be expressed by

$$\sigma = a^2/D^2 \tag{1}$$

$$e = aN_A\sigma \tag{2}$$

$$D = a\sqrt{\frac{aN_A}{e}} \tag{3}$$

where D is the average distance between junction points of the copolymer.

The equilibrium average brush height (L) of the segment which is in the good solvent can also be related to σ. From scaling arguments based on the blob picture, de Gennes[13] predicted that

$$L \cong a_B N_B \sigma^{1/3} \tag{4}$$

Figure 1 gives a physical representation of the three relevant parameters for the MJL model, i.e., e, D, and L.

The MJL theory describes the adsorption regimes (mentioned earlier) as a function of three conditions. The first condition is a measure of the asymmetry of the polymer chain (β), the second is related to the surface density of the molten layer (σ), and the third to the spreading power of the surface (S), i.e., a measure of the interactions between the particulate, the A block, and the solvent. The β parameter is given by:

$$\beta = R_B/R_A = N_B^{3/5}/N_A^{1/2} \tag{5}$$

and β is frequently referred as the asymmetry parameter.

In our previous work, it was shown that one can conveniently discuss the surface properties of any material in term of its acid/base characteristics and relate these characteristics to the wettability of a surface.[7,8] This relation is not unreasonable, since an IGC study by Lara and Schreiber[6] showed that the adsorption of various polyesters on a wide variety of organic pigments was greatly influenced by the acid/base interactions present in the polymer/particulate pair. Using the theory proposed by Gutmann,[14] one can assign to a material an acceptor number (AN) and donor number (DN). The AN characterizes the acidity or the electron-acceptor ability, while the DN defines the basicity or the electron-donor ability of a material. A high AN value indicates that the material is acidic, while a high DN value implies that it is basic. As was discussed in ref 9, the asymmetry of the units used to define AN and DN by the Gutmann theory imposes limitations on the interpretations of values obtained by IGC. Nevertheless, IGC remains one of the most convenient techniques for a relatively rapid evaluation of internally consistent parameters expressing the acid/base interaction potential of solids. The relative acidity or basicity of a material can be conveniently expressed by the AN/DN ratio. Using the results obtained from the previous studies in this series,[7-9] one can calculate the AN/DN ratio for the particulates studied here, which will be an indication of the relative interaction potential of the substrates.

Table I. Characteristics of the Copolymer Diblocks

S-4VP sample	label	S units (number average)	PI for the styrene block	4VP units (number average)	PI for the copolymer diblock
family	S-4VP1	180	1.24	11	1.21
	S-4VP2			29	1.21
	S-4VP3			73	1.22
	S-4VP4			190	1.31
1[a]	S-4VP5	575	1.14	85	1.20
2[a]	S-4VP6	930	1.13	82	1.15

[a] Samples were synthesized by S. Varshney.

The present study investigates, by ^{1}H NMR, the adsorption of styrene-*b*-4-vinylpyridine [P(S-*b*-4VP)] copolymer onto several particulates in a selective solvent, i.e., toluene-d_8. The investigated parameters are the type of particulate (in term of its acid/base properties) and the chain lengths of the two dissimilar segments, i.e., the styrene and 4-vinylpyridine blocks of the copolymers. The experimental results are then compared with the predictions obtained from the model proposed by Marques et al. for the VDWB regime.[11]

2. Experimental Section

2.1. Polymer Synthesis. Anionic polymerization is the favored method for the synthesis of block copolymers of very well-defined architecture, molecular weight, and narrow molecular weight distribution.[15] However, these desirable properties are only achieved under rigorously controlled synthetic conditions involving the exclusion of air, water, and any contaminants that would either interfere with or terminate the normal propagation of the living anionic polymer chains.

The apparatus, as well as the polymeriztion, the isolation, and characterization of the materials, is described in detail elsewhere.[16,17] The diblock copolymers were synthesized by sequential anionic polymerization of the styrene monomer followed by the 4-vinylpyridine monomer (4VP), using *n*-butyllithium as initiator. The polymerization details specifically for the present system were given in one of our previous papers.[7]

The molecular weights of the polystyrene blocks were determined by size-exclusion chromatography (SEC) using a Varian 5000 LC. The solvent was THF at 50 °C, and standardization involved five monodisperse PS references (Varian TSK kit). Analyses were performed in duplicate, with a precision of the order of 5%. The vinylpyridine content was determined by a nonaqueous titration using a solution of perchloric acid in glacial acetic acid according to established procedure.[18] The polydispersity index of the copolymer diblock was determined by SEC in *N*-methylpyrrolidinone at 90 °C.[19]

The copolymer diblocks used in this work are listed in Table I, which summarizes the composition of the diblocks and the polydispersity index of the styrene (S) block and of the diblock. The samples identified by an asterisk in Table I were synthesized by Dr. Sunil Varshney. These samples were synthesized using a procedure similar to that described in ref 7, but using a different

Table II. Specific Areas and Interaction Properties of the Substrates (Combined from refs 5–7).

particulate	label	specific area (m^2/g)	AN	DN	AN/DN
Chromosorb W[5]	C-1	1.0	2.1	0.3	7.0
rutile 1 (TiO_2)[6]	R-1	10	10	3.7	2.7
rutile 2 (TiO_2)[6]	R-2	8.8	7.3	4.8	1.5
$CaCO_3$[7]	C-2	3.3	7.1	8.7	0.8

apparatus.[17] The polydispersity index (PI) was found to be less than 1.2 for the styrene blocks. For all the copolymer diblocks, the polydispersity index was found to be of the order of 1.2. In the case of samples S-4VP1 to S-4VP3, the PI value of the diblock is significantly smaller than that of the parent S block. This implies that the 4VP block has a reasonably narrow distribution. To illustrate the abbreviations that will be used throughout this paper, S-4VP1 [180–11] indicates a PS chain length of 180 units joined to a 4VP chain of 11 units. For 4VP1 to 4VP4, the 1 after the VP indicates the first member of the family of increasing VP chain lengths, 2 indicates the second, etc.

2.2. Substrates. Four particulates were used in this study as substrates for the adsorption of the copolymer diblocks. The first is a chromatographic support that was previously used in the work described in ref 7, i.e., Chromosorb W (C-1). The BET surface area for this particulate is 1 m^2/g. The characterization of the acidic and basic rutiles (R-1, R-2) is described in ref 8. The rutile R-1 and R-2 were known to be surface coated by the supplier (Tioxide Canada) and to have a BET surface area of 10 and 8.8 m^2/g, respectively. The $CaCO_3$ (C-2), from ICI Inc., has a surface area of 3.3 m^2/g, again as evaluated by the BET method. Table II summarizes these characteristics, as well as the interaction potentials of the particulates described in terms of their acidity and basicity numbers (AN, DN), and their relative interaction potentials (AN/DN).

2.3. NMR. The NMR spectra were acquired on a Varian 300XL spectrometer using a standard pulse sequence (S2PUL) with 128 transients. The NMR samples were prepared from stock solutions (0.05 g of diblock/2 mL of toluene-d_8). Various quantities of these solutions were then placed in the NMR tube, and toluene-d_8 was added to a total volume of 1.0 mL. In all the cases the diblock concentrations ranged from 0.2 to 35 mg/mL. The ^1H spectrum for these solutions was acquired at 25 °C. Figure 2a shows a typical spectrum of S-4VP in tetrahydrofuran-d_8, along with an identification of the peaks. As will be explained later, for a ^1H spectrum in toluene-d_8, the region of interest is in the aliphatic region of the spectra, i.e., 7.5 to 9 τ (Figure 2b).

To these solutions was added 0.1 g of dried particulates. As was suggested by Blum et al.,[20] these solutions were then sealed and left for more than 24 h in order to obtain equilibrium adsorption (7 days were used in this study). During that period, most of the samples became clear because the particulates settled to the bottom of the tube. If they did not, a centrifuge was used to accelerate the process. The ^1H spectra for each solution were then acquired.

From the ^1H spectrum of the S-4VP3 [180-79] diblock in THF-d_8 (Figure 2a) one can calculate the unit ratio of 4VP to the total repeat units by dividing the area of signal A by signal C + D (3.2–3.8 τ) or F + F′ (8.3–8.8 τ). A comparison of the VP fraction obtained by NMR with that obtained by titration, shows a discrepancy of less than 1% between the two methods [0.291 from A/(C + D) or 0.289 from A/(F + F′) vs 0.289 by titration]. This indicates that a precise concentration of polymer diblock (or area ratio) can be calculated. In order to ascertain the reproducibility of the technique, the tubes containing samples with a polymer concentration of 10 mg/mL were analyzed in triplicate for each particulate. For each of the four particulates, the adsorbed quantities of copolymer diblock were repeatable to better than 4%. Thus, one can expect that the experimental error in the concentration is less than 5%.

For the ^1H spectrum (in toluene), the signal arising from the CH_2 groups (F + F′, 8.2–8.7 τ) of the S-4VP was chosen to determine the total polymer concentration (Figure 2b), since no other signal overlaps with it. In order to ascertain that the area of CH_2 groups will be comparable between the two spectra, i.e., with or without particulates, one must use an internal standard, since the relative intensity can differ between spectra. The area of the residual signal originating from the protonated or partly protonated CH_3 groups of the toluene-d_8 was chosen as the internal standard. Using the area ratio of the CH_2 groups to the internal standard enables one to compare normalized intensities.

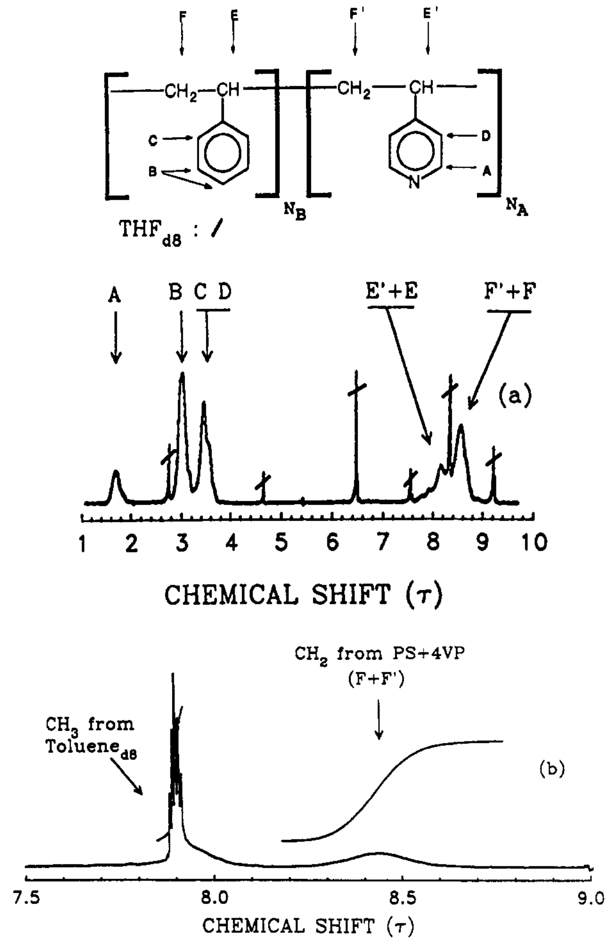

Figure 2. Typical ^1H spectrum at 25 °C for the S-4VP3 [180-73] copolymer diblock: (a) whole spectrum in THF-d_8 (/), (b) enlargement of the aliphatic region (7.5–9 τ), in toluene-d_8.

In view of the previous discussion, the concentration of the S-4VP for the adsorption isotherm is determined as follows: First the area ratio of the CH_2 groups of the S-4VP to the internal standard is calculated for the spectra with the particulates (R_p) and without them (R_o). Then the quantity of S-4VP adsorbed on the particulates can be calculated from the following equation:

$$\text{weight of diblock adsorbed} = W_o \times [1 - (R_p/R_o)] \qquad (6)$$

where W_o is the initial weight of diblock in solution.

The normalized quantity of adsorbed copolymer (per unit area of substrate) can then be obtained by dividing result of eq 6 by the specific area of the substrate.

3. Results and Discussion

This discussion is subdivided into five sections. The first section will be devoted to the description of the adsorption isotherms and to the method of evaluation of the 4VP thickness (e) from the normalized equilibrium quantity of adsorbed material (Q_{eq}*). In the second section, a justification will be given for the use of the van der Waals–Buoy regime to describe the present systems. The subsequent two sections contain a brief discussion of the influence of the lengths of S-4VP blocks on the adsorption, and of the agreement between the experimental e values and those calculated from the MJL model. Finally, the last section will establish the relation between the Q_{eq}* values and the acid/base properties of the substrates, and also relate the latter to the prefactor of the MJL scaling model.

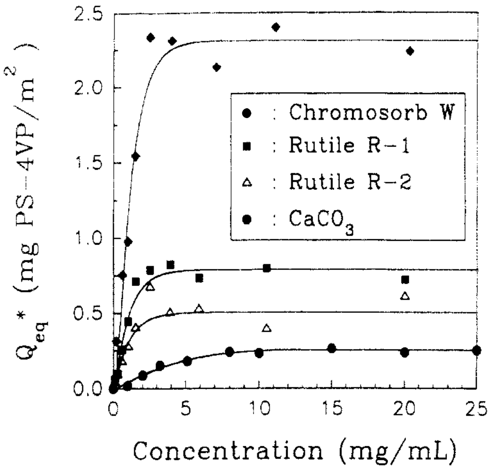

Figure 3. Adsorption isotherms for S-4VP3 [180-73] on various particulates in toluene-d_8 at 25 °C: ◆, Chromosorb W (C-1); ■, rutile 1 (R-1); △, rutile 2 (R-2); and ●, $CaCO_3$ (C-2).

3.1. Adsorption Isotherms. The determination of the normalized quantities of adsorbed diblocks on the particulates was explained in the data-treatment section. The adsorption isotherms for the four particulates are shown in Figure 3 for polymer S-4VP3 [180-73]. From this plot one can see that as the concentration of the diblocks in solution increases, the quantity of adsorbed polymer initially increases and then reaches a plateau value. That plateau value is the equilibrium quantity (Q_{eq}*) of diblock adsorbed per square meter of the surface. This Q_{eq}* value varies with the type of particulate. For example, the Q_{eq}* for the Chromosorb W (C-1) is 2.2 mg/m^2, or ca. 3 times that for rutile R-1 of 0.8 mg/m^2.

To calculate the thickness of the adsorbed 4VP layer, the Q_{eq}* (g/m^2) is multiplied by the weight fraction of the VP in the copolymer [$f_{VP} = N_A MW_A/(N_A MW_A + N_B MW_B)$], and then divided by the density of the 4VP (ρ), which, after normalization of the units, yields the desired number. This is summarized in eq 7.

$$e_{4VP\ exp} = Q_{eq}^* \text{ (g/m}^2) \times f_{VP} \times 1/\rho \text{ (cm}^3\text{/g)} \times 10^6 \text{ (m}^3\text{/cm}^3) \times 10^{10} \text{ (Å/m)} \quad (7)$$

The calculation yields 4VP thickness (e) values of 6.4, 2.3, 1.5, and 0.7 Å for the particulates C-1, R-1, R-2, and C-2, respectively. It is clear that the amount of base (4VP) adsorbed on a substrate should be related to the acidity of the substrate, and this is, indeed, the case. These low e values indicate that the S-4VP forms, at most, a monolayer on these particulates in toluene solution. These calculations were repeated for all the other particulate/copolymer systems studied here. The values obtained with eq 7 do not account for the swelling of VP segments by the toluene-d_8 solvent. For the MW range of VP blocks used in this study, it is known that the solvent uptake can be as high as 50% v/v^2, and since the density of both components are close to unity, the values obtained with eq 7 should be multiplied by a factor 2 to account for the presence of the toluene. In order to keep this discussion as general as possible, and since information about solvent uptake is not readily available for many systems, the e values were deliberately not corrected. This has very little effect on the general analysis; however, one must keep in mind that the reported e values, as well the prefactor in eq 10 (k), would have to be modified by a factor 2.

3.2. The van der Waals–Buoy Regime. In order to find out which of the regimes discussed above best represents the present system, one must determine which set of conditions associated with a particular regime is met by the S-4VP/particulate systems. The relevant numbers here are the asymmetry of the blocks (β), the surface density of the molten layer (σ), and the wetting ability (S) that exist between the substrate and the anchor.

Table III. Relevant Parameters for the MJL Model for the Adsorption of Diblocks in Selective Solvent

S-4VP sample	R_B (Å)	R_A (Å)	β	$N_A^{3/5}$	σ (×10^4)	$N_B^{-6/5}$ (×10^4)	f_{VP}
S-4VP1	41	8	5.1	4.2	290	20	0.058
S-4VP2	41	14	2.9	7.5	180	20	0.14
S-4VP3	41	21	2.0	13	110	20	0.29
S-4VP4	41	35	1.2	23	67	20	0.52
S-4VP5	82	23	3.6	14	77	4.9	0.13
S-4VP6	110	23	4.8	14	68	2.7	0.081

In the present study, the VDWB regime was chosen, since all the conditions are met by the present diblock/substrate systems. Specifically, for a VDWB regime, the following conditions must be met:

$$\text{(a)}\quad 1 < \beta < N_A^{3/5}$$

$$\text{(b)}\quad \sigma > N_B^{-6/5}$$

$$\text{(c)}\quad S > 0$$

The first two conditions are specifically related to the architecture of the copolymer diblock, and will be treated first. The relevant quantities needed to verify the first two conditions are reported in Table III. As can be seen in that table, these two conditions are fulfilled by all but one of the copolymer diblocks, the exception being the S-4VP1 sample, for which $\beta > N_A^{3/5}$. However, for sake of completeness, since two out of three conditions are met by that sample, it will also be analyzed with the equations associated with the VDWB regime. The third condition (c) states that favorable interactions must exist between the anchor and the particulate (i.e., good wettability between the two) in order to result in specific adsorption of the VP segments. As will be shown later, the AN/DN ratios can be used to express the acid/base properties of the particulates; they can also be used to characterize polymers. In the previous work,[7] various polymers were characterized in bulk by IGC, and the AN/DN ratios were determined to be 0.6 and 0.3 for the PS and the 4VP homopolymers, respectively. The absolute values of the indices suggest that the 4VP is a strong base, while the PS is only mildly basic. Thus, from simple acid/base considerations, one can expect that the 4VP will be preferentially adsorbed onto acidic or mildly basic substrates, such as $CaCO_3$. In the previous studies, it was, indeed, shown that for copolymer diblocks of P(S-*b*-4VP) of various block lengths, the VP segments were preferentially orienting toward the surface of the particulates.[7,8] Moreover, Tsai et al.[5] studied very similar block copolymers of P(S-*b*-2VP) adsorbed onto silver surfaces. Using techniques such as Raman and angle-resolved X-ray photoelectron spectroscopy, the authors confirmed that, for the P(S-*b*-2VP) copolymer diblocks, the 2VP block was preferentially adsorbed onto the surface, while the PS block was positioned away from the surface. They also found that for adsorbed P2VP and P4VP homopolymers, the orientation of the VP rings was, to some extent, different, even though the ring could be considered to be perpendicular to the surface in both cases. This suggests that, for these systems, favorable interactions exist between the VP anchor and the substrate, and by extension, that $S > 0$. Most likely the same kind of behavior can be expected in a selective solvents, since the 4VP segment, being in a hostile environment, will prefer to stay close to the wall of the substrate.

For the VDWB regime, the three relevant parameters (e, L, and D) shown in Figure 1 can be calculated. The equations derived by MJL[11] for this regime are

$$e \cong N_A^{11/23} N_B^{-6/23} \tag{8}$$

$$L = a_{PS} N_B^{21/23} N_A^{-4/23} \tag{9}$$

The expression for D was already given in eq 3. The relation described by eq 8 is crucial, since by multiplying the right-hand side of this equation by a scaling prefactor (k), one can obtain the theoretical layer thickness. This can by expressed by equation 10.

$$e = k N_A^{11/23} N_B^{-6/23} \tag{10}$$

The MJL theory does not consider the prefactor k. However, by comparing the values of the 4VP thicknesses calculated from the isotherms with the number obtained from evaluation of the right-hand side of eq 8, the value of the prefactor k in eq 10 can easily be evaluated with a curve-fitting program. The nonlinear curve-fitting program from Sigmaplot was used for that purpose (to determine the optimal value of k). The calculated k values for R-1 and R-2 are 1.1 and 0.68, respectively (correlation coefficient > 0.990 in both cases). These numbers will be discussed in the two following sections.

In the discussion above, it was shown that the general MJL model applies reasonably well to the S-4VP systems studied here. However, finer details of the MJL theory can be explored, since more suitable scaling expressions have been derived by Parsonage et al.[2] for similar systems. The authors studied P(S-*b*-2VP) (abbreviated as S-2VP) copolymer diblocks adsorbed onto mica or oxidized silicon substrates from toluene solution. They applied the MJL theory to their system and did the analysis in terms of a normalized dimensionless surface density (σ^*). The authors related the σ^* parameter to the σ of the MJL model for the VDWB regime with the following set of equations:

$$\begin{gathered} \sigma = Q_{eq}{}^* N_{Av} / (MW_A + MW_B) \\ \sigma_{ol} = 1/(\pi R_B{}^2) \qquad (11) \\ \sigma^* = \sigma/\sigma_{ol} = \pi a_B{}^2 \sigma N_B{}^{6/5} \end{gathered}$$

where N_{Av} is the Avogadro's number, σ_{ol} is the surface density above which the PS blocks are overlapping (forming a semidilute solution in the adsorbed layer), and R_B represents the radius of gyration of the PS blocks in dilute toluene solutions. The data for R_B was obtained from the work of Higo et al.,[12] i.e., $R_B = a_B N_B \nu$; $a_B = 1.86$ Å, $\nu = 0.595$. In terms of the σ^* parameter, they obtained the following expression for the asymmetry ratio (β):

$$\beta = N_B^{6/5} / N_A^{2/3} \tag{12}$$

For the S-2VP block copolymers adsorbed onto mica, the authors showed that the log–log plot of σ^* vs β was linear for β values ranging from 10 to 100, implying that the MJL VDWB regime was valid for that range. The same type of plots can be constructed to demonstrate that the MJL VDWB regime is suited for the present S-4VP systems. The σ^* and β values, along with the other relevant parameters, were calculated for all the S-4VP diblocks adsorbed on various substrates, and are reported in Table IV.

Table IV. Relevant Parameters for the MJL Model As Expressed by Parsonage et al.[2]

substrate	VP units (N_A)	PS units (N_B)	β	coverage (mg/m^2)	σ (m^{-2} × 10^{-16})	σ_{ol} (m^{-2} × 10^{-16})	σ^* (σ/σ_{ol})
R-1	11	180	100	1.70	5.1	1.9	2.7
R-1	29	180	54	1.10	3.0	1.9	1.6
R-1	73	180	29	0.78	1.8	1.9	0.95
R-1	190	180	15	0.70	1.1	1.9	0.58
R-2	73	180	29	0.50	1.1	1.9	0.58
R-2	85	575	105	0.90	0.78	0.48	1.6
R-2	82	930	190	1.10	0.62	0.27	2.3
C-1	73	180	29	2.20	5.0	1.9	2.6
C-2	73	180	29	0.25	0.57	1.9	0.30
C-2	29	180	54	0.33	0.88	1.9	0.48

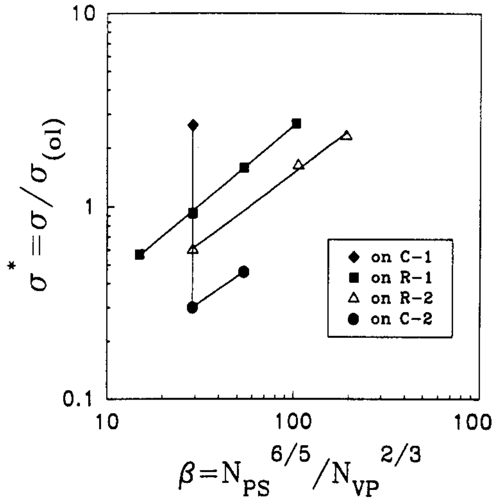

Figure 4. log–log plots of the dimensionless surface density (σ^*) against the asymmetry ratio (β) for the S-4VP samples adsorbed onto various substrates from toluene: ◆, Chromosorb W (C-1); ■, rutile 1 (R-1); △, rutile 2 (R-2); and ●, $CaCO_3$ (C-2).

The log–log plots of σ^* vs β are shown in Figure 4. From this figure, one can see that the σ^* values for the different particulates fall on approximately parallel lines. Moreover, there is very little evidence of curvature in those plots, even for S-4VP [930-82] (β = 190). From these plots, it is clear that σ^* varies with the asymmetry of the copolymer, as well as the type of substrate onto which the diblock copolymer is adsorbed (the vertical line connects the results for the S-4VP [180-73] sample). Thus, it seems reasonable to consider that all the samples can be described by the MJL VDWB regime.

Arguably, one can say that from the present study no direct information is obtained to ascertain the validity of the scaling relation for the PS brush (eq 9). However, if this relation holds, a log–log plot of $L/(a_{PS}N_{PS})$ vs σ should yield a linear relation with a slope equal to 1/3 ($L = N_{PS}^{21/23} N_{VP}^{-4/23} a_{VP}$ and $\sigma = \sigma^*/(\pi a_{PS}^2 N_{PS}^{6/5})$). Figure 5 shows these plots for the S-4VP systems investigated in the present study, as well as the results ($\beta < 100$) from the work of Parsonage et al.[2]

The plots show that the relation is linear for the four systems (correlation coefficient > 0.986). The slope of these plots varies from 0.29 to 0.36 (≅1/3), which indicates that, within experimental error, the scaling relation is valid for the four systems. Moreover the relative positions of these plots are consistent with the acid/base properties of the substrates; i.e., from $CaCO_3$ (AN/DN = 0.8) to mica (AN/DN ≅ 5), they decrease as the relative acidity of the substrate increases. In view of the above evidence, the S-4VP systems belong the MJL VDWB regime, and the relation $L \propto a_B N_B \sigma^{1/3}$ holds. Thus, the scaling relations derived from the MJL model are valid and can be applied in the present work.

3.3. Influence of the P4VP Block Length on the Adsorption. In performing this study, two factors must

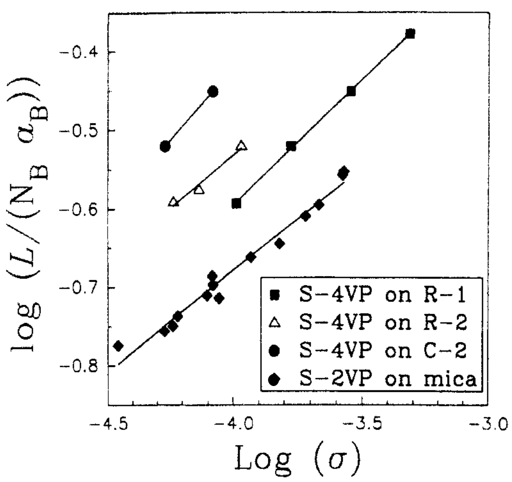

Figure 5. log–log plots of the equilibrium average PS brush height ($L = a_BN_B^{21/23}N_A^{-4/23}$) divided by a_BN_B against the surface density (σ) for the S-4VP systems. Additional data for the S-2VP systems were obtained from ref 2: ◆, mica; ■, rutile 1 (R-1); △, rutile 2 (R-2); and ●, $CaCO_3$ (C-2).

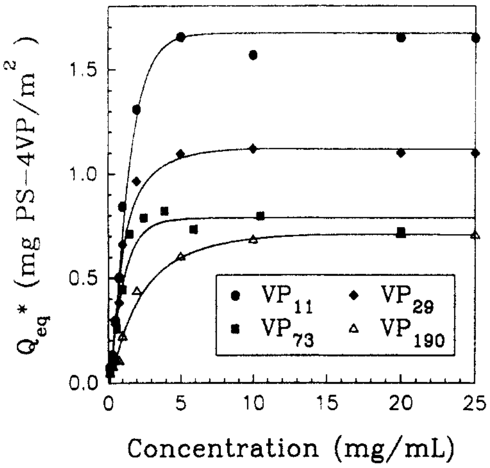

Figure 6. Adsorption isotherms for the S-4VP family on R-1 in toluene-d_8 at 25 °C: ●, S-4VP1 [180-11]; ◆, S-4VP2 [180-29]; ■, S-4VP3 [180-73]; △, S-4VP4 [180-190].

be taken into account. For convenience, the AN/DN ratio of the substrate should be as high as possible to maximize the quantity of adsorbed polymer. Furthermore, the density of the substrate must be high in order to minimize the volume of pigment inside the NMR tube. The rutile R-1 was selected for this study, since its density (≅4 g/cm^3) is much greater than that for the particulate C-1 (≅0.5 g/cm^3) and its AN/DN value is greater than that for R-2 or C-2.

Four samples were used to study the influence of the 4VP anchor on the adsorption of the S-4VP. These samples ranged in 4VP block length from 11 to 190 units, and are identified in Table I as S-4VP1 to S-4VP4. The styrene block length was kept constant at 180 units. The adsorption isotherms are shown in Figure 6. This figure shows that the Q_{eq}* of the adsorbed diblock increases as the anchor length decreases. This behavior is reasonable, since for the short 4VP segments, a greater total quantity of polymer can be adsorbed, provided that the 4VP is long enough to anchor the diblock to the surface. Furthermore, the excluded area on the surface of the substrate decreases as the 4VP anchor length decreases. This leads to the effective increase for the observed Q_{eq}* values with decreasing 4VP block lengths, since a larger quantity of material can be adsorbed per unit area of substrate. This behavior is also expected from the MJL theory, since as the 4VP chain length decreases, the size of the "blob" of S-4VP decreases in parallel. This implies that for short 4VP anchors, more "blobs" (more diblock chains) will be adsorbed on the surface than in the case of long VP anchors. The Q_{eq}* values are reported in Table V, along with those obtained for the study of the influence of the PS block length. This table also summarizes the calculations of the relevant MJL parameters (*e*, *D*, and *L*) for both series of samples.

For the four samples studied here (S-4VP1 to S-4VP4), the *e* values determined from the adsorption isotherms are 0.98, 1.5, 2.3, and 3.5 Å, respectively. The comparison of these *e* values with those calculated from eq 10 ($k = 1.1$ in Table V) shows that the correlation between the two sets of data is good. Thus, the 4VP chain length study clearly shows that good agreement exists between the experimental *e* values and those obtained from MJL theory using the prefactor *k*.

3.4. Influence of the PS Block Length and the Substrate on the Adsorption. In the previous section, the value of the prefactor *k* (eq 10) was determined for S-4VP/rutile R-1 systems. For this part of the study, another substrate (R-2) was selected, since that allows the determination of *k* for the material. It was previously shown that the rutile R-1 was the most convenient substrate, and therefore it was selected for the first part of the study described earlier. Using the same criteria, the rutile R-2 was determined to be the second best substrate, and for this reason it was selected for the present part of the study. Three samples were used in order to determine the influence of the PS chain length on the adsorption isotherms, i.e., S-4VP3, S-4VP5, and S-4VP6, since their 4VP anchor is relatively constant at 80 units and the PS length varies from 180 to 930 units (see Table I). From the adsorption isotherms (Figure 7), one can see that an increase in the PS chain length leads to an increase in the Q_{eq}* of the adsorbed diblock. This indicates that the PS chain length has an influence on the adsorption of the 4VP segment, as expected by the MJL model. For the three samples, this suggests that the VP coverage will be thicker for shorter PS chains. This behavior is clearly illustrated in Table V by the significant decrease in the *e* value from sample S-4VP3 [180-73] to S-4VP5 [575-85] and on to S-4VP6 [930-82].

For this system, the *k* value determined by the curve fitting program was found to be equal to 0.68. As can be seen in Table V, the calculated *e* values (eq 10) agree well with the experimental *e* values. This indicates that the MJL model again fits the experimental results. It should be noted that the *k* value for R-2 (0.68) is smaller than that evaluated in the previous section for R-1 (1.1). While the MJL model does not evaluate the prefactor, in the present study we have the opportunity of doing so by relating the prefactor to some measurable experimental quantities, and this will be the subject of the next section. This was obviously the reason for selecting another substrate for this part of the study.

3.5. Relation between the Prefactor and the Acid/Base Properties of the Substrates. For the isotherms shown in Figure 3, only the type of particulate was varied (S-4VP3 [180-73]). The difference in the Q_{eq}* values for the different particulates must be related to differences in the spreading power of the surface (*S*). As was mentioned earlier, *S* can be discussed in term of the acid/base characteristics of the substrate, which are related to the interaction potential, i.e., the AN/DN ratio. The AN/DN ratios for the particulates were reported in Table II and are included in Table VI. This table also summarizes the Q_{eq} values, the Q_{eq}* values, and the experimental *e*

Table V. Comparison of the Thickness of the Film Obtained from Adsorption Isotherms with Those from the MJL Model for Various Copolymers on R-1 or R-2

			from experimental isotherms		from MJL theory[c]			
					e (Å)			
S-4VP sample	Q_{eq}[a]	Q_{eq}*[b]	*e* (Å)	*D* (Å)	*k* = 1.1 for R-1	*k* = 0.68 for R-2	*D* (Å)	*L* (Å)
				Substrate R-1				
S-4VP1 [180-11]	17	1.7	0.98	13	0.93		13	140
S-4VP2 [180-29]	1	1.1	1.5	17	1.5		17	120
S-4VP3 [180-73]	7.8	0.78	2.3	22	2.3		22	100
S-4VP4 [180-190]	7.0	0.70	3.5	29	3.6		29	86
				Substrate R-2				
S-4VP3 [180-73]	4.4	0.50	1.4	29		1.4	29	100
S-4VP5 [575-85]	8.0	0.90	1.1	34		1.1	34	280
S-4VP6 [930-82]	9.5	1.1	0.87	38		0.94	38	440

[a] Q_{eq} = mg of S-4VP/g of rutile. [b] Q_{eq}* = mg of S-4VP/m^2. [c] The 4VP thicknesses values were determined via eq 10, and the prefactor (*k*) value was evaluated with the curve-fitting program.

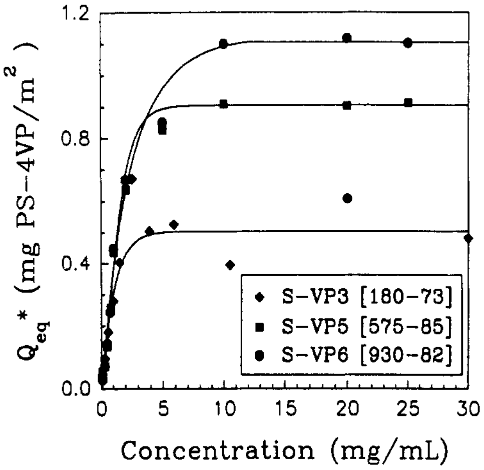

Figure 7. Adsorption isotherms for the S-4VP samples with a relatively constant 4VP anchor on R-2 in toluene-d_8 at 25 °C: ◆, S-4VP3 [180-73]; ■, S-4VP5 [575-85]; ●, S-4VP6 [930-82].

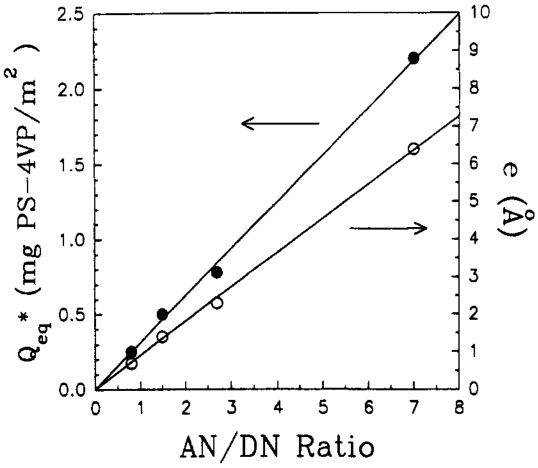

Figure 8. Relation between the acid/base properties of the particulates and the Q_{eq}* of S-4VP3 adsorbed (●) and the thickness of the 4VP layer (○).

Table VI. Relation between the Acid Base Properties of the Particulates and the Normalized Adsorbed Equilibrium Quantities of Diblocks (Q_{eq}*) for S-4VP3 [180-73]

particulate	AN/DN	Q_{eq}[a]	Q_{eq}*[b]	*e* (Å)
Chromosorb W	7.0	2.2	2.2	6.4
rutile-1 (TiO_2)	2.7	7.8	0.8	2.3
rutile-2 (TiO_2)	1.5	4.4	0.5	1.5
$CaCO_3$	0.8	0.8	0.25	0.7

[a] Q_{eq} = mg of S-VP3/g of particulate. [b] Q_{eq}* = mg of S-VP3/m^2.

values for the four substrates. The table shows that the relative acidity of the particulates decreases from Chromosorb (7) to $CaCO_3$ (0.8), in parallel with the Q_{eq}* values. This suggests that as the favorable interaction between the surface and the nitrogen ring increases (from $CaCO_3$ to Chromosorb), the thickness of the VP coverage also increases. This behavior indicates that a more efficient packing of the 4VP rings can be achieved with highly interacting surfaces. It is clear that the amount of base (4VP) adsorbed on a substrate should be related to its acidity, and this is indeed the case here.

In order to obtain a quantitative relation between the acid/base properties of the surface and the adsorbed quantity of the 4VP anchor, plots were prepared of the Q_{eq}* and the *e* values against the AN/DN ratios. These plots are given in Figure 8. The plot of Q_{eq}* versus the AN/DN ratio is linear, with a slope of 0.31 and a correlation coefficient of 0.9988. The intercept was set to 0. For the plot of AN/DN vs *e*, only the slope differs (0.91), since *e* is obtained by multiplying Q_{eq}* by a constant. Such a correlation between these parameters implies that the acid/base characteristics of the particulate are linearly related to the amount of adsorbed 4VP. This finding also confirms that the spreading power of the surface can be conveniently expressed by the ratio of the acidic and basic sites present on the surface of the particulate as measured by the AN/DN ratio.

Before proceeding, one must explore more extensively the physical significance of the prefactor in eq 10. We know that *S* is related to the AN/DN ratios. However, as was shown in Figure 8, the AN/DN ratio is also related to *e* for a specific polymer system. Moreover, eq 10 from the MJL theory clearly shows that *e* is related to *k*. Therefore, the AN/DN ratios must be related to the prefactor. From Figure 8, the prefactor *k* of the MJL theory can be expressed by eq 13.

$$k = \frac{\Phi_1}{\Phi_0 \times K} = \frac{\Phi_1}{2.7 \times 0.91} \qquad (13)$$

K is the slope of the line (open circles, slope = 0.91), Φ_0 = 2.7 is the AN/DN ratio of the rutile R-1, and Φ_1 is the AN/DN ratio for any of the other substrate under investigation. The rutile R-1 was arbitrary selected as Φ_0, since the substrate has been used for most of the systems in this study.

In order to illustrate the empirical relation (eq 13) between the acid/base properties and the prefactor, a plot was prepared of the experimental *e* values (from Table V) against the values calculated with $(\Phi_1/\Phi_0)N_A^{11/23}N_B^{-6/23}$. This plots is given in Figure 9. This figure can also be used to improve the *K* value by using the curve-fitter program (described earlier) to recalculated it. The new value was found to be equal to 0.88. As can be seen in

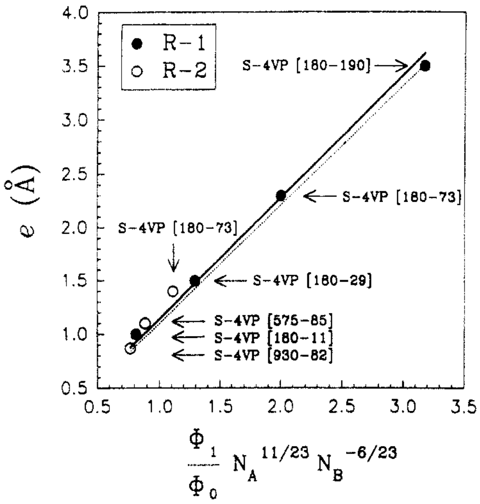

Figure 9. Illustration of the agreement between the experimental 4VP thickness and that calculated from eq 13 with $k = \Phi_1/(\Phi_0 K)$. The solid line was plotted with the K value obtained with the curve fitting program (0.88), while the dotted line used the K value from the slope of Figure 7 (0.91).

Figure 9, for both K values a good agreement was found between the calculated e values (eq 13) and those obtained experimentally. Thus, it clear that the prefactor can, indeed, be described in term of the acid/base concept.

Provided that the AN and DN indices for the investigated substrates are known, this relation can be useful for workers in the field of composites, since from a single isotherm determination, one can predict the thickness of the adsorbed layer for a wide variety of particulate systems for the S-4VP diblock copolymer. Naturally, the concept can also be extended to other block copolymers. On a given substrate, using a well-characterized diblock, the Q_{eq}* can be obtained from the adsorption isotherm. Application of eq 7 yields the thickness of the adsorbed layer for this diblock. From the experimental e value, the prefactor of eq 10 can be calculated, since the K_1 value of eq 13 can be obtained by setting the AN/DN ratio of this particular substrate to Φ_1 and assigning the AN/DN ratio of another particulate to Φ_0. Using the k value obtained via the acid/base properties, eq 10 can be used to predict the experimental e values of any diblock on any particulate. Evidently, from that predicted e value, the Q_{eq}* value can be back-calculated. Thus, for the VDWB regime, one can predict, from a single isotherm run, the adsorption behavior for any copolymer diblock/substrate systems.

4. Conclusion

In this paper, a study is reported of the adsorption of S-4VP diblocks on to various particulates in a selective solvent. This study shows that NMR is an excellent tool for the determination of the quantities of diblock copolymers in solution. Specifically, the NMR technique can be used to establish adsorption isotherms, which generally require techniques that are more tedious (weighing) or more complex (isotope assay techniques). In this work, the 4VP coverage formed by the adsorption was characterized. It was established that the acid/base properties of the particulates greatly influence the adsorption of the 4VP anchor and that a linear relation exists between the AN/DN ratios and the thickness of the 4VP coverage, which has a thickness of the order of angstroms. As might be expected, the thickness of the 4VP coverage increases as the relative number of acid sites increases on the surface of the particulate. This behavior suggests that a more efficient packing of the 4VP rings is achieved with highly interacting acidic surfaces.

Good agreement was found between the 4VP coverage thickness obtained by the MJL model (eq 10) and that calculated from the adsorption isotherms. It was found that the quantity of adsorbed material was linearly related to the intrinsic acid/base properties of the particulates, and that the prefactor in the MJL theory is directly related to the acid/base indices (AN/DN ratios). An equation is proposed which quantifies this relationship. This equation allows one to predict the thickness of the adsorbed layer for a wide variety of particulates and diblock copolymer systems from a single isotherm determination and gain knowledge of the AN and DN indices of the substrates.

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