Interfacial Properties of a Diblock Amphiphilic Copolymer: Poly(isobutylvinyl ether-*b*-2-methyl-2-oxazoline)

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ABSTRACT: Novel amphiphilic diblock copolymers, poly(isobutylvinyl ether-*b*-2-methyl-2-oxazoline) (PIBVE-*b*-POXZ), were synthesized by cationic polymerization. The molar ratio of IBVE in the copolymers was varied from 20% to 50%. Their molecular weights were over the range from 1000 to 4000. The associations of these copolymers have been studied by small-angle neutron scattering (SANS) in two selective solvents: water which solubilizes the POXZ block and cyclohexane which solubilizes the PIBVE block. In 1% solutions, all the soluble copolymers formed micellar aggregates. The copolymers have been adsorbed on porous silica particles from selective and nonselective solvents. The adsorbed layers have been studied by SANS. In the case of a nonselective solvent of the two sequences (dichloromethane) copolymers have shown comparable adsorption as the homopolymers. Influence of concentration of solutions has been studied in adsorption from aqueous solutions. For dilute watery solutions, the adsorbed chains were in mushroom configuration and the adsorbed amounts were low. On the opposite, stable and very dense copolymer layers corresponding to extended brushes have been obtained in the presence of concentrated watery solutions. The copolymer chains are anchored by the PIBVE blocks which are collapsed on the surface while the POXZ blocks are in a very extended conformation. The influence of the hydrophilic/lipophilic balance has been studied by varying the chemical composition. The amounts of adsorbed polymer were increased with amount of IBVE in the copolymer. The thicknesses of the adsorbed layers have been found to follow qualitatively the theoretical model of Marques and Joanny for the adsorption of diblock copolymers in selective solvents. Adsorption from cyclohexane which is a selective solvent of the PIBVE block at different copolymer compositions has shown thick adsorbed layers which could correspond to direct adsorption of the micelles on the surface.

Introduction

The adsorption of macromolecules plays a vital role in various applications: stabilization of colloidal particles, flocculation, dispersion processes, biological applications, adhesion, and separation process.[1−3] Therefore, the adsorption phenomena and surface studies of these polymers are of great interest both experimentally and theoretically. In particular, in the case of diblock copolymers, surface modification can be tailored in different ways depending on the multiple block−surface and block−solvent interactions. Indeed, these copolymers may be adsorbed selectively according to the nature of the solvent. In a block-selective solvent, which is a good solvent for one block but poor for the other, a diblock copolymer may deposit out on a solid substrate which is in contact with the polymer solution.[4−10] If the interaction between the insoluble polymer and the solid surface is favorable, a dense polymeric monolayer called a polymer brush may form. In a polymer brush, the insoluble block spreads on the solid surface like a melt and the soluble block stretches into the solution-like bristles of a brush. In a nonselective solvent, the organization of the adsorbed layer will depend strongly on the surface selectivity for one or the other block.[11−13] In all the cases of solvent qualities, the interfacial architectures will also show a great dependence to the relative length of the blocks. Indeed, for chains having relatively long anchor blocks, the adsorption mechanism should be controlled by the energy of the anchoring layer whereas for chains with symmetric blocks or with relatively long buoy blocks, the elastic energy of the buoy layer should play an important role in the copolymer adsorption.

The aim of the following paper is to study the interfacial architectures of a family of diblock copolymers poly(isobutylvinyl ether-*b*-2-methyl-2-oxazoline) as a function of the solvent quality and copolymer composition: (a) in a nonselective solvent, dichloromethane, the higher affinity of the surface for the poly-2-methyl-2-oxazoline block (POXZ) drives the adsorption mechanism; (b) in water, which is a selective solvent of the POXZ block, brush structures constituted of a molten PIBVE layer spreading on the solid surface and an extended POXZ buoy layer are obtained; (c) in cyclohexane, a selective solvent of the PIBVE block, the copolymers have relatively longer insoluble blocks (POXZ) and still show thick adsorbed layers.

The diblock copolymers have been designed for surface modification applications in biological systems. The poly(2-methyl-2-oxazoline) block is nonionic and hydrophilic and shows comparable properties as poly(ethylene oxide), particularly its good biocompatibility has been investigated in refs 14−16. The polyisobutylvinyl ether block adds its hydrophobicity to form an amphiphilic copolymer. Block copolymers of varying compositions: containing 20−50% IBVE units, are obtained by cationic polymerization in a one-batch process. The synthesis is made by sequential monomer addition because both

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monomers polymerize by a living mechanism and the first living polymer is an initiator for the second polymerization.[17]

The experimental technique small-angle neutron scattering (SANS) has been used to study the interfacial copolymer layers. The copolymers were adsorbed on porous silica particles. The silica dispersions were analyzed in mixtures of deuterated−hydrogenated solvents in order to match the neutron scattering length density. Adsorbed amounts and thicknesses of the adsorbed layers were determined from these experiments. The copolymer solution have also been studied by SANS, to characterize the copolymers and their associations in selective solvents.

The paper is organized as follows: the synthesis and characterization of the copolymers is described in the first part. The second part is devoted to the studies of the copolymer solutions in the two selective solvents: water and cyclohexane. The aim is to demonstrate that the copolymers are associated in micellar structures under the conditions of adsorption, as the adsorption mechanism is depending upon the conditions of associations. Adsorption of the copolymers in the three different solvents (dichloromethane, water, cyclohexane) will be studied and the results discussed in the last part.

Experimental Section

Materials. The monomers isobutylvinyl ether (Aldrich, purity 99%) and 2-methyl-2-oxazoline (Aldrich, purity 99%) were dried overnight over calcium hydride and purified by distillation under a nitrogen atmosphere. Hexane (SDS), dichloromethane (SDS), and acetonitrile (SDS) were distilled over calcium hydride before use. Anhydrous hydrogen iodide as hexane solution or dichloromethane solution were obtained by the dehydration of commercial hydriodic acid (Aldrich, 57% in water) using phosphorus pentoxide following literature procedure.[18] Iodine (Aldrich) was purified by sublimation under vacuum and stored as a dichloromethane solution. Ammonia, a 2.0 M solution in ethanol (Aldrich), was used as purchased.

Syntheses. Polymerization of 2-Methyl-2-oxazoline. The cationic polymerization of 2-methyl-2-oxazoline was initiated with the hydrogen iodide−iodine system under a nitrogen atmosphere. The polymerization was carried out at 80 °C in acetonitrile. The polymerization was stopped by pouring 2.0 mol·L^{-1} ammonia solution in ethanol into the reaction mixture.

Polymerization of Isobutylvinyl Ether. The isobutylvinyl ether was polymerized in hexane at −20 °C or in dichloromethane at −30 °C. The initiation and the quenching of polymerization were performed in the same way as for the polymerization of 2-methyl-2-oxazoline.

Synthesis of Diblock Copolymers. The block polymerization of isobutylvinyl ether and 2-methyl-2-oxazoline have been investigated in hexane and dichloromethane.[17] Initiation was carried out by using the hydrogen iodide−iodine system in dichloromethane. Isobutylvinyl ether was polymerized first at −20 °C in hexane or −30 °C in dichloromethane under nitrogen atmosphere. After complete consumption of this monomer, 2-methyl-2-oxazoline and acetonitrile were added to the living polyisobutylvinyl ether chain. The polymerization of the second monomer was carried out at 80 °C. The copolymerization was quenched with addition of ammonia, a 2.0 M solution in ethanol.

Characterization of Polymers. ^{1}H NMR spectroscopy were performed at 200 MHz on a Brücker instrument in dissolving polymers in deuterated chloroform.

Size exclusion chromatography was performed on a chromatograph equipped with a pump P 100 (Spectra-Physics), a Rheodyne injector, and different sets of columns. The detectors connected at the end of the columns were a differential refractometer RI 71 (Shodex) and a MiniDawn light scattering detector (Wyatt Technology). The MiniDawn instrument uses a polarized semiconductor diode laser (λ = 690 nm) and measures the scattered light at three angles (45, 90, and 135°). The homopolymers of 2-methyl-2-oxazoline were characterized in an aqueous 0.1 mol·L^{-1} $LiNO_3$ solution with a PL-aquagel OH-40 column (Polymer Laboratories). The polyisobutylvinyl ethers were analyzed in tetrahydrofuran with a set of two columns PL-gel Mixed C (Polymer Laboratories). The characterization of copolymers was carried out in chloroform with a set of three columns PL-gel 5μ: 500, 10^3, and 10^4 Å (Polymer Laboratories). The calibration of columns in organic solvents was made with a set of polystyrene standards with a range of molecular weight from 580 to 2 × 10^6.

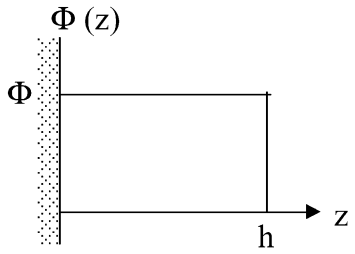


Figure 1. Step function model.

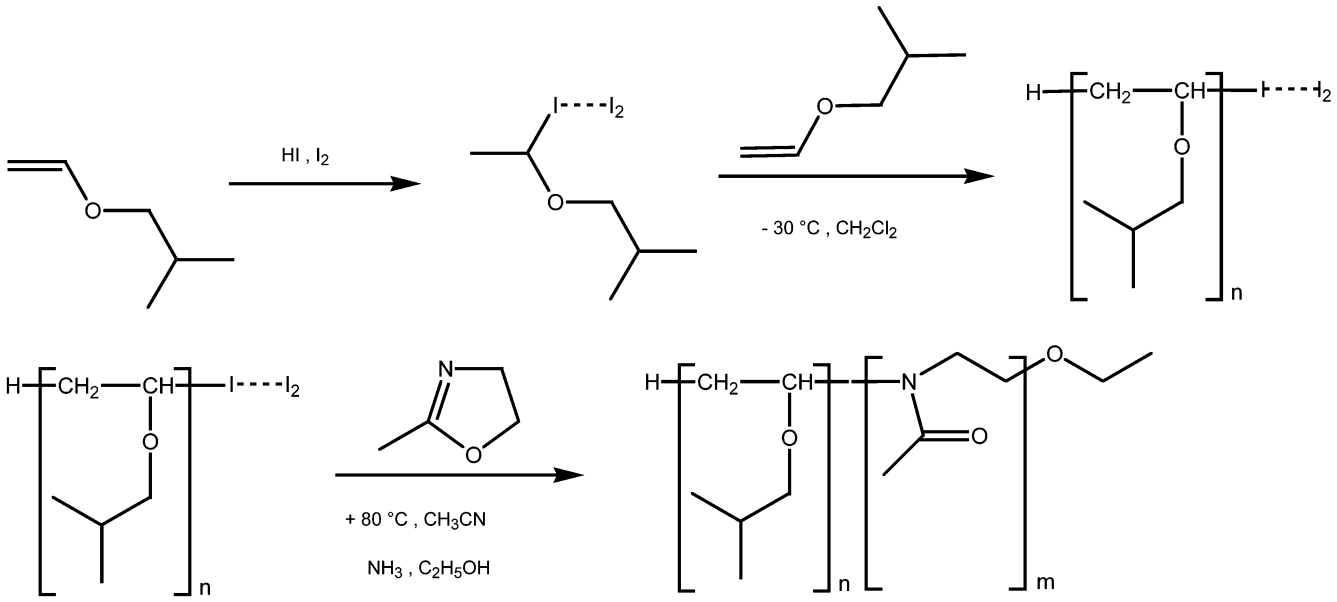
Polymer in Solution. The behavior of polymers was studied in different solvents: dichloromethane, water and cyclohexane. Dichloromethane is a solvent of both block, water and cyclohexane are selective solvents for POXZ block and PIBVE block, respectively. The polymer solutions had concentration of 1 wt % and were analyzed by small-angle neutron scattering (SANS).

Adsorption of Copolymers. The silica particles (CPG, Fluka) used for adsorption experiments were porous particles with a particle diameter of 10 μm and a pore diameter of 3000 Å (surface area 6.9 m^2/g and pore volume 0.77 cm^3/g, given by manufacturer). The concentration of the copolymer solutions was fixed to 2 wt % to ensure that the surface was saturated. The copolymers solutions were adsorbed with a fixed ratio polymer/silica of 0.2 (w/w) during 24 h. Then the supernatant was extracted and the silica particles were rinsed several times with pure solvent or mixtures of deuterated/non deuterated solvent in the case of neutron scattering experiments. Mixtures containing 6.3% CH_2Cl_2/93.7% CD_2Cl_2 were used for studies in dichloromethane in order to obtain a contrast matching of the silica. In water, the silica contrast matching solvent was: 41.7% H_2O/58.3% D_2O whereas in cyclohexane the matching solvent mixture was 45% C_6H_{12}/55% C_6D_{12}.

Neutron Scattering Measurements. Small-angle neutron scattering (SANS) measurements were performed at the Laboratoire Léon Brillouin (" ORPHEE " reactor, CEN Saclay) on the " PACE " spectrometer. The scattering vector length q ranges from 10^{-3} to 10^{-1} Å^{-1}. Neutron wavelength of 6 Å was collected using a distance sample−detector configuration of 3.2 m. The samples were loaded into Hellma quartz neutron cells with a 2 mm optical path length. The cells were placed in a sample changer and the scattering for each sample was measured for about 4 h at 20 °C. The temperature was controlled to ±1 °C. The scattering length density of the POXZ and PIBVE blocks have been calculated assuming densities equal to 1 for both polymers: $n_{POXZ} = 1.10 \times 10^{10}$ cm^{-2}, $n_{PIBVE} = 4.82 \times 10^8$ cm^{-2}. The theory of the small-angle neutron scattering (SANS) applied to adsorbed polymer, the experimental procedures, and the analysis of the data have been widely described in the literature.[19−21] A short theoretical background with the equations used in the present work is given in this section.

A great advantage of neutron scattering lies in the possibility of contrast variation. Indeed, by using a suitable isotopic mixture of fully hydrogenated-fully deuterated solvent, it is possible to match the "neutral refractive index" of the silica. Under that condition, the scattering intensity comes only from the adsorbed polymer. The spectra were analyzed directly (as they were obtained) in using a step function model (Figure 1) for the interfacial density profile $\Phi(z)$, which is not an a priori

Scheme 1



assumption for the shape of $\Phi(z)$ but rather provides a useful tool for comparing the data. The scattering intensity of this step is, at contrast matching:

$$I(q) = 2\pi\left(\frac{S}{V}\right)(n_p - n_s)^2\, q^{-4} 2(1 - \cos qh)\Phi_s^2 \qquad (1)$$

where $I(q)$ is measured in absolute scale (cm^{-1}), q the scattering vector, S/V the specific surface, n_p (or n_s) the scattering length density of the polymer (or solvent), h the thickness of the layer, and Φ_s the fraction of the surface occupied by the polymer. Equation 1 could be rewritten as

$$q^4 I(q) = 2\pi\left(\frac{S}{V}\right)(n_p - n_s)^2 2(1 - \cos qh)\Phi_s^2 \qquad (2)$$

which is a purely oscillating term. A Taylor expansion of (1) leads to

$$q^2 I(q) = 2\pi\left(\frac{S}{V}\right)(n_p - n_s)^2\gamma^2\left[1 - \frac{q^2h^2}{12}\right] \qquad (3)$$

for very small q, where $\gamma = \int_0^h \Phi(z)\, dz$ (in Å). γ can be easily converted into the amount of polymer per unit area (in mg/m^2), $\Gamma = 0.1\gamma d$, where d is the density of the polymer (in g/cm^3).

Therefore, two plots are useful: $q^4 I(q)$ vs q, which emphasizes the possible discontinuities of the density profile (the solid−polymer and the polymer−solvent boundaries) and $q^2 I(q)$ vs q^2, which allows the determination of two basic parameters: Γ and h. The amount of adsorbed polymer Γ was determined by the extrapolated scattered intensity I at q close to zero, and the slope of the linear regime is related to the thickness of the polymer layer h.

Results and Discussion

Synthesis of Polymers. Block copolymers were obtained by cationic polymerization in a one-batch process. The synthesis was made by sequential monomer addition with the hydrogen iodide-iodine system as initiator (Scheme 1). First, the monomer IBVE was polymerized. After complete consumption of this monomer, the end of this chain plays the role of initiator for the polymerization of the second monomer 2-methyl-2-oxazoline. Experimental conditions of synthesis were reported in Table 1. In a previous paper,[17] we described in details this synthesis. We showed that some secondary reactions, depending on temperature and solvent polarity, occurred during propagation of the chain polymerization of IBVE. Therefore, the copolymers obtained had a red color.

Table 1. Experimental Conditions of Synthesis[a]

	block IBVE			block OXZ		
polymer	solvent	temp (°C)	time (h)	[OXZ]/[HI]	temp (°C)	time (h)
POXZ 1				30	80	24
POXZ 2				30	80	28
A1[b]	C_6H_{14}	−20	24	20	80	65
A2[b]	C_6H_{14}	−20	24	20	80	24
A3[c]	CH_2Cl_2	−30	0.5	30	80	24
A4[c]	CH_2Cl_2	−30	0.5	30	80	24
A5[c]	CH_2Cl_2	−30	0.5	30	80	48
A6[c]	CH_2Cl_2	−30	0.5	30	80	24
PIBVE 1	C_6H_{14}	−20	24			
PIBVE 2	CH_2Cl_2	−30	1			

[a] $[HI]_0 = 30.5$ mmol·L^{-1}; $[I_2]_0 = 6.1$ mmol·L^{-1}; $[IBVE]_0 = 0.63$ mol·L^{-1}. [b] $[OXZ]_0 = 0.86$ mol·L^{-1}. [c] $[OXZ]_0 = 0.55$ mol·L^{-1}.

Table 2. Characterization of Polymers

polymer	% IBVE	M_w^{SEC} (g mol^{-1})	I_p^{SEC}	M_w^{SANS} (g mol^{-1})[c]	R_g (Å)[c]	$N_{PIBVE} - N_{POXZ}$
POXZ 1	0	4000[a]	1.08	3150	32	0−37
POXZ 2	0	7300[a]	1.40	7330	123	0−86
A2	20	1000[b]	2.4	3780	24	9−34
A6	27	1700[b]	1.7	2630	16	8−22
A3	30	1400[b]	1.5	1690	15	5−12
A4	37	1300[b]	1.8	1830	11	7−12
A5	46	4000[b]	2.1	3130	18	16−18
A1	50	3100[b]	3.2	5000	30	26−26
PIBVE 1	100	3100[b]	1.1	2830	17	28−0
PIBVE 2	100	2600[b]	1.08			26−0

[a] M_w measured by MiniDawn instrument. [b] M_w measured using polystyrene standards calibration curve. [c] Values determined by SANS in CD_2Cl_2.

Characterization of Polymers. All the characterization results were reported in Table 2. The composition of copolymer in PIBVE was determined by ^{1}H NMR spectrum from the ratio $r = i/(i + j)$. The values i and j were calculated from the integrated peaks 1 and 2 from the ^{1}H NMR spectrum (Figure 2). Block copolymers having 20−50% of IBVE were synthesized.

SEC analysis, performed with different column/solvent combinations, compatible with the polymers or

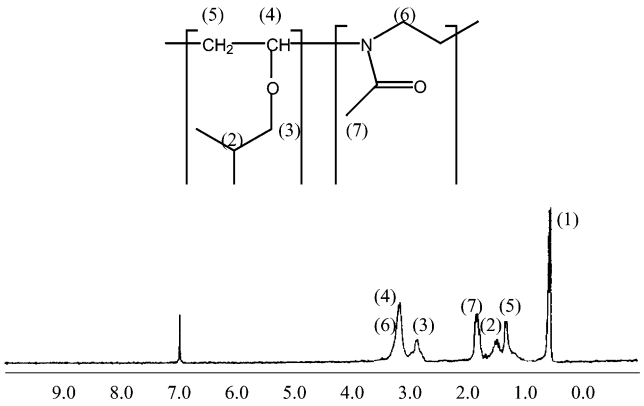


Figure 2. ^{1}H NMR spectra of copolymer A1.

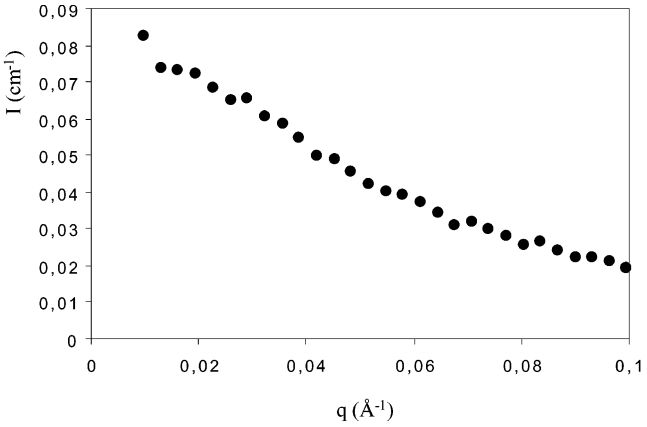


Figure 3. Scattering from copolymer A1 in CD_2Cl_2.

copolymers under study, allowed determination of molecular weights. The results are summarized in Table 2. Different methods of detection were used: absolute from light-scattering detection or relative from calibration curve with standards. For polyisobutylvinyl ether, we have previously shown that molecular weight measured by a light-scattering detector was in good agreement with the molecular weight determined from polystyrene calibration curve.[17] In Table 2, the molecular weight of POXZ were measured by a light-scattering detector and the molecular weight of polyisobutylvinyl ether and copolymers were determined from the polystyrene calibration curve. The copolymers could not be analyzed with the light-scattering detector at $\lambda = 690$ nm because of their absorption at this wavelength (red color of copolymers).

The polymers and copolymers were also characterized by SANS in CD_2Cl_2 which is a solvent of both blocks. Figure 3 shows the SANS scattering intensity $I(q)$ as a function of q obtained from copolymer A1 in CD_2Cl_2. At small angles, the scattering intensity can be approximated by the Zimm equation, eq 4a, or by the Guinier equation, 4b, yielding an overall apparent radius of gyration:

$$\frac{1}{I} = \frac{1}{I_0}\left(1 + \frac{R_g^2}{3}q^2\right) \tag{4a}$$

$$\ln I(q) = \ln I_0 - \frac{R_g^2}{3}q^2 \tag{4b}$$

This is illustrated in Figure 4 where $1/I$ is plotted against q^2 and where only the linear part of the

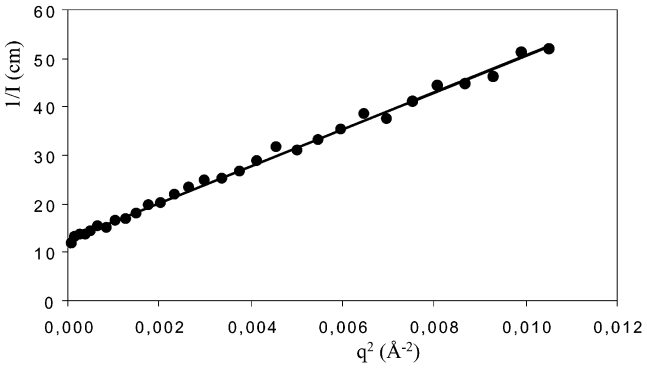


Figure 4. Plot $1/I$ vs q^2 for copolymer A1 in CD_2Cl_2.

scattering data has been taken into account for the analysis. From the extrapolated scattered intensity at q close to zero I_0, the molecular weight of homopolymers was calculated according eq 5 and 6.

$$I_0 = \Phi \frac{N_{PIBVE}}{v_{PIBVE} + \frac{N_{POXZ}}{N_{PIBVE}}v_{POXZ}} \times \left[v_{PIBVE}(n_{PIBVE} - n_s) + \frac{N_{POXZ}}{N_{PIBVE}}v_{POXZ}(n_{POXZ} - n_s)\right]^2 \tag{5}$$

where Φ is the volumic fraction, v_{PIBVE} and v_{POXZ} are the partial volumes of a unit, and N_{PIBVE} and N_{POXZ} are the unit numbers of each comonomer.

$$M_w = N_{PIBVE}M_{IBVE} + N_{POXZ}M_{OXZ} \tag{6}$$

M_{OXZ} and M_{IBVE} are the molar masses of OXZ and IBVE units, respectively. The results are listed in Table 2. For the same molecular weight, POXZ had a higher R_g than PIBVE. The apparent R_g values for the copolymers ranged from 11 to 30 Å, depending on composition and molecular weight.

The molecular weights determined by SEC and SANS can be compared from Table 2. The values are generally in good agreement except for copolymers A2 and A6. This discrepancy seems to be related to copolymer composition: indeed copolymers A2 and A6 contain a high proportion of POXZ block. SEC analysis of the copolymers were perfomed in $CHCl_3$ which is a good solvent of both blocks. However homopolymer of POXZ have shown some interaction with the column (PL-gel) in this solvent. Copolymers with a higher POXZ fraction should interact more strongly with the column than copolymers with a lower POXZ fraction. This explains the result obtained with copolymers A2 and A6: due to their interaction with the column, they were eluted later than expected from a pure size exclusion mechanism. Copolymer A1, which is larger than the other copolymers, shows also a weaker discrepancy between the SEC and SANS determinations. This resulted in apparent molecular weights lower than the one extracted from the SANS measurements. Because of this residual POXZ/column interaction, the M_w^{SANS} values will be used in the following for characterization of the copolymers.

Polymers in Selective Solvents. Diblock copolymers in selective solvents have been extensively studied during the past decade.[22] The copolymers are believed to form micellar aggregates above a critical concentration, the core corresponding to aggregated insoluble

Table 3. Polymer in D_2O

polymer	% IBVE	R_g^{app} [a] (Å)	R_g^{core} [b] (Å)	R_g^{shell} [c] (Å)	N^{ag} [d]	e^{shell} (Å)	l_c (Å)
A2	20	58	53	74	49	21	127
A6	27	71	65	120	136	55	81
A3	30	88	80	129	333	50	44

[a] D_2O. [b] 24% D_2O/76% H_2O. [c] 9% D_2O/91% H_2O. [d] N^{ag} is the aggregation number of the aggregates, determined from intensity at low q in D_2O, $e^{shell} = R_g^{shell} - R_g^{core}$, and $l_c = (N_{POXZ}a)$ is the contour length of the POXZ blocks.

blocks. Water and cyclohexane are two opposite selective solvents since water is a solvent of POXZ (non solvent of PIBVE) and cyclohexane is a solvent of PIBVE. Aggregation of the polymers in these two solvents has been studied in order to correlate the solution and the interfacial structural properties.

Polymers in D_2O. The hydrophobic microdomains are made up of PIBVE blocks. Solvatation of the aggregates is ensured by a hydrated POXZ shell. Aqueous polymer solutions (1 w/w) have been studied by SANS as a function of the copolymer composition. Copolymers with PIBVE molar ratio larger than 46% were only partially soluble and their associations in solution have not been characterized. Guinier plots (eq 4) allowed to extract the apparent radius of gyration of the aggregates and the limiting intensities I_0. Assuming low interaction between the micelles, aggregation numbers (N^{ag}) have been calculated from eq 5, N_{PIBVE} and N_{POXZ} being replaced by N^{ag}_{PIBVE} and N^{ag}_{POXZ}, the numbers of IBVE or OXZ units per aggregate. The results are reported in Table 3. There is an increase of R_g^{app} with increased IBVE molar ratio of the copolymers. Calculated aggregation numbers increase qualitatively in the same way. Assuming that R_g^{app} is mostly related the radius of gyration of the core (which will be verified later), $(R_g^{app})^3$ will be proportional to the volume of the core and thus to the aggregation number only if the micelles are spherical. However $N^{ag}/(R_g^{app})^3$ increase also with the IBVE molar ratio, contrary to the behavior expected from a simple model of non interacting spherical micelles.[23] Either non-negligible interactions between micelles, or change of micellar shapes (transition from spheres to rods) could be responsible for this behavior.[4]

To characterize more properly the aggregates, contrast matching conditions of the micellar core or shell were used. Copolymers were dissolved in mixed solvents: 91% H_2O/9% D_2O in order to study the POXZ shell, and 76% H_2O/24% D_2O in order to study the PIBVE core. The radius of gyration of the cores and shells determined from Guinier plots are reported in Table 3. The core radius are in good agreement with the apparent radius of gyration (without contrast matching conditions), showing that most of the micellar scattering is produced by the cores. Because of high incoherent scattering, it was not meaningful to study the form factor on the available q range. The radius of gyration of the cores (values comprised between 50 and 80 Å) are much larger than the contour lengths of the PIBVE blocks (values comprised between 13 and 22 Å). This behavior can be attributed to nonspherical shapes for the micelles. Indeed the Guinier plots show anisotropic particle shapes for the three samples (the Guinier plot of copolymer A3 is shown in Figure 5) with upward deviations to the Guinier straight lines. In another hand, the large core radius can also be attributed to the partial swelling of the core by the solvent.[24−27] The shell

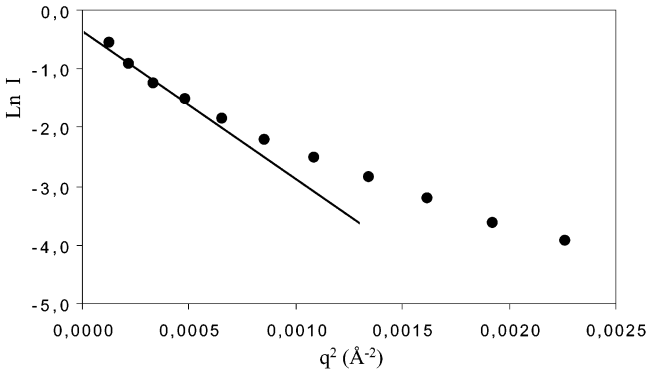


Figure 5. Guinier plot of copolymer A3 in mixed solvent of 76% H_2O/24% D_2O.

Table 4. Polymer in C_6D_{12}

polymer	% IBVE	R_g^{app} (Å)	N^{ag}	l_c (Å)
A3	30	158	2200	44
A4	37	94	590	47
A5	46	77	280	69

thicknesses $e^{shell} = (R_g^{shell} - R_g^{core})$ give the extension of the POXZ blocks in the shells. These values can be compared in Table 3 to the contour length of the POXZ blocks: $l_C = (aN_{POXZ})$, where N_{POXZ} is the number of segments in a POXZ block and a is the monomer size ($a = 3.75$ Å). For copolymer A2, having the lowest IBVE content, the POXZ blocks have a conformation close to a Θ solvent. The average distance between POXZ blocks on the surface of the core can be estimated from the value of the aggregation number ($N^{ag} = 49$) and the radius of gyration of the core (53 Å). This value, 26 Å, is found to be of the same order as e^{shell}. Consequently, the POXZ blocks are not expected to interact in the shell and this is coherent with the finding of their coiled conformation. On the contrary, the shell thicknesses are larger for copolymers A3 and A6. The POXZ blocks are almost completely extended, and this is well correlated with higher aggregation numbers. Brush structure are obtained in these cases.

Polymer in C_6D_{12}. Cyclohexane is a good solvent for PIBVE and a nonsolvent for POXZ, leading to micelles made of a core of POXZ and a shell of PIBVE: the symmetric situation compared to water. However, there is not a real symmetry in the solubility of the copolymers as a function of their composition in cyclohexane and in water: 80% POXZ are necessary to reach the solubility limit of copolymers in cyclohexane (copolymer A2) while the limit in water is reached for copolymer containing more than 46% PIBVE (copolymer A1). The higher solubility in cyclohexane than expected, make us think that the POXZ core of the micelles should be partly swollen with the solvent. As was done in water, polymer solutions (1%) have been studied by SANS. Guinier plots allowed to extract the apparent radius of gyration which are reported in Table 4. The apparent radius of gyration decreased when PIBVE molar ratio was increased. Aggregation numbers, calculated in the same way as was done in aqueous solutions, show also a significant decrease with PIBVE molar ratio. Quite unusually high values of the aggregation numbers obtained for copolymers A3 and A4 (Table 4) are an indication that nonspherical aggregates should be formed in this composition range. This is well correlated with high values of the apparent radius of gyration, larger than the contour length of the POXZ blocks which constitute the core of the micelles (see Table 4).

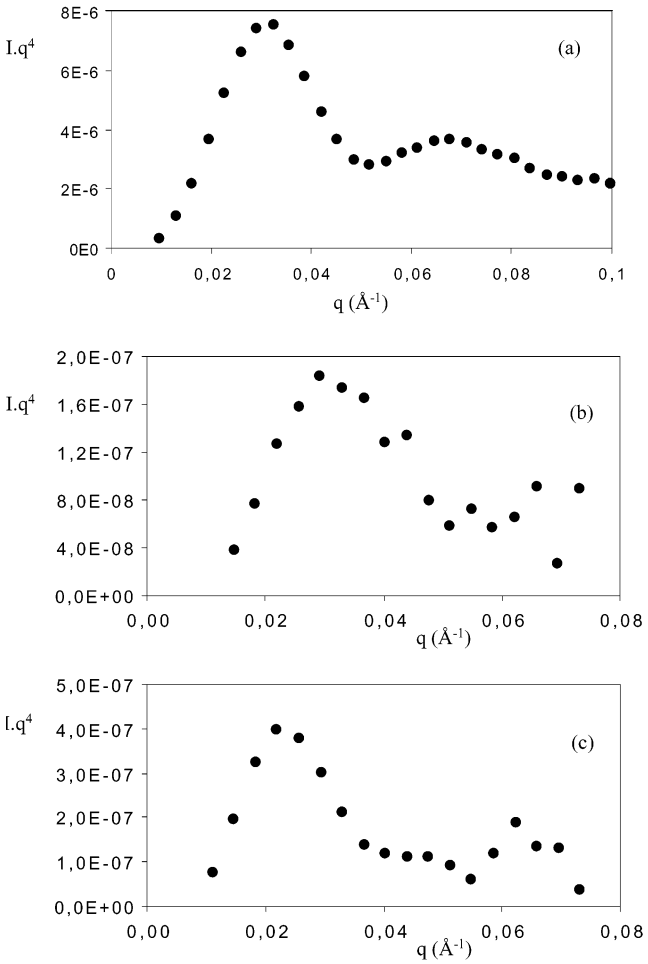


Figure 6. Scattering from copolymer A5: (a) in C_6D_{12}, (b) in mixed solvent of 95,3% C_6H_{12}/4,7% C_6D_{12}, and (c) in mixed solvent of 80.1% C_6H_{12}/19.9% C_6D_{12}.

For copolymer A5, diffusion by the core and by the shell have been studied independently by using mixed solvents in contrast matching conditions. Figure 6 shows Iq^4 as a function of q in the three conditions of contrast: pure C_6D_{12}, 95.3% C_6H_{12}/4.7% C_6D_{12} (same contrast as the shell), and 80.1% C_6H_{12}/19.9% C_6D_{12} (same contrast as the core). In pure C_6D_{12}, as well as in 95.3% C_6H_{12}/4.7% C_6D_{12}, intensity plots have been well fitted by the form factor of a dense sphere, radius of gyration $R_g = 76$ Å, and radius of the sphere 102 Å. As was noted for micelles in water, most of the micellar scattering is produced by the core. The radius of a compact sphere made of 280 POXZ blocks is 64 Å, lower than the determined core radius (102 Å). This proves that the micellar cores are not a melt of POXZ but are partly swollen with the solvent: for copolymer A5, 80% of the core's volume should be filled with solvent.

Adsorption in Dichloromethane. Dichloromethane is a nonselective solvent in which PIBVE and POXZ are equally soluble. Both polymers can make hydrogen bonds with the surface groups: the adsorption can occur by hydrogen bonding of the ether group of PIBVE, or carbonyl group of POXZ with the surface silanol groups. The latter group is known to make stronger interactions with the surface than the previous one.[3] Adsorption of both polymers on silica are thus expected. Adsorbed layers have been studied by neutron scattering experiments on the silica dispersions. Figure 7 shows the typical shape of the SANS results, namely $\ln(I(q)q^2)$ vs

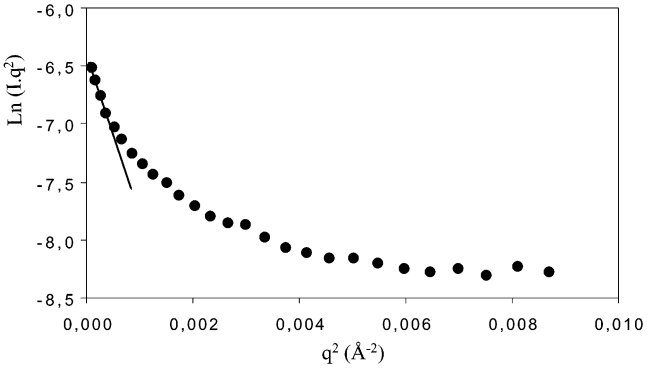


Figure 7. Variation of $\ln[Iq^2]$ vs q^2 from CD_2Cl_2 solution of copolymer A1 adsorbed on silica.

Table 5. Adsorption in Dichloromethane

polymer	% IBVE	Γ (mg·m^{-2})	h (Å)
POXZ 1	0	2.8	52
POXZ 2	0	2.1	
A2	20	1.2	48
A6	27	1.1	51
A3	30	1.0	42
A4	37	1.0	46
A5	46	1.2	58
A1	50	1.8	
PIBVE 2	100	0.9	38

q^2 where only the linear part of the scattering data has been taken into account for the analysis. Adsorbed amounts and thicknesses of the layers have been extracted using eq 3, and the results are reported in Table 5.

For POXZ homopolymers, quite large adsorbed amounts have been measured: around 2−3 mg/m^2. These values are more than two times larger than the one reported for the adsorption of similar polymers polyethyloxazoline and polymethyloxazoline from water or ethanol.[11,28] More generally,[3] polymers interacting via hydrogen bond with the surface usually show adsorbed amounts in the range 0.5−1 mg/m^2. Polymer−polymer interactions in the adsorbed layer could be responsible for these high adsorbed amounts. Adsorption isotherm of POXZ in dichloroethane has been performed with another kind of silica particles: nonporous silica aerosol 200 (Degussa) following a method described in ref 29. A plateau adsorbed amount at 1 mg/m^2 was reported.[30] It corresponded to the following conditions: adsorption concentration 1% w/w and a ratio (total polymer weight)/(total silica surface) = 2.5 mg/m^2. In the case of the neutron scattering experiments with the porous silica particles, the adsorption concentration was larger (2% w/w) and the ratio (total polymer weight)/(total silica surface) = 29 mg/m^2 was about 10 times larger. These conditions could have induced a different adsorption regime, by favoring polymer−polymer interactions in the vicinity of the surface.

In the case of PIBVE, the obtained adsorbed amount (0.9 mg·m^{-2}) was in agreement with the general expectations of a polymer interacting via hydrogen bonds with the surface.

The two blocks of the copolymers compete for the surface sites. A high difference in adsorption energy of the segments is expected between PIBVE and POXZ blocks, in favor of the latter one. Model of block copolymer adsorption in nonselective solvent predict structural properties of the layers as a function of copolymer composition.[12] Predicted adsorbed amounts

are comparable to the homopolymer values in a wide range of composition, except in the domain of copolymer rich in the less interacting block. Higher adsorbed amounts can be obtained in this domain, the maximum being obtained for an optimum composition depending on the interaction parameters and copolymer molecular weight.[12] Polyoxazoline rich copolymers (containing 54−80% of POXZ segments) show a comparable adsorption as for PIBVE with adsorbed amounts on the order of 1 mg/m^2 and layer thicknesses of about 50 Å. The adsorbed amount is close to 2 mg/m^2 for copolymer A1. The increased adsorption for this sample can be well accounted for by the model of Evers and colleagues,[12] assuming a much higher surface affinity for the POXZ block than for the PIBVE block: maximum adsorbed amounts are predicted for contents in the strongly adsorbing block slightly larger than 50% for chains of low molecular weights like in this study. Bijsterbosch and colleagues[11] studied the adsorption of block copolymers from a nonselective solvent (water), poly(2-methyl-2-oxazoline-*b*-ethylene oxide), and poly(2-ethyl-2-oxazoline-*b*-methyl vinyl ether). They found maximum adsorbed amounts for compositions rich in the strongly adsorbing block, contrary to the result of the present study. They concluded that their results were not in disagreement with SCF model of Evers and colleagues but corresponded to a low difference between the segmental adsorption energies of the two blocks. Comparison of our results with the results of ref 11 shows that polymethyloxazoline has a large difference in segmental adsorption energies with polyisobutylvinyl ether but a low difference with poly(ethylene oxide) (one should keep in mind that the solvents are different in the two experiments). Steric hindrance which disfavors hydrogen bonding with the ether groups of IBVE should explain this behavior.

Adsorption in Water. Water is a selective solvent of the POXZ blocks. The PIBVE blocks, insoluble in water, anchor the copolymer by collapsing on the surface. The amount of adorbed polymer by unit area Γ and the thickness of the adsorbed layer h have been determined at low scattering vector q and under contrast matching conditions with the silica as described in the Experimental Section. The scattered intensity plotted as $\ln(I(q)q^2)$ vs q^2 for a copolymer A1 containing 50% of IBVE adsorbed from solutions at two different concentrations are reported in Figure 8. When the polymer solution concentration (Figure 8a) was small the nonmonotonic variation of $\ln(Iq^2)$ as a function of q^2 indicated that the layer was not homogeneous.[7] The adsorbed amount, on the order of 1 mg/m^2, was comparable to the one obtained for the homopolymer POXZ (see Table 6). The chain density per surface unit is then too low to induce a brush structure and the adsorbed chains are in a mushroom configuration. At concentrations of adsorption larger than 1%, homogeneous and dense layers are obtained (adsorbed amount 7,9 mg/m^2). A typical plot is shown in Figure 8b for a concentration of 2%. Oscillations are observed on a plot of $q^4I(q)$ as a function of q (Figure 9). These oscillations look like interference fringes and prove the existence of two well-defined boundaries: a solid−polymer and a polymer−solvent discontinuity. This behavior is not observed for homopolymer adsorbed layers where the polymer density is expected to decrease more smoothly with the distance to the surface.[31] Figure 9 shows the characteristics of a steeper density profile and is indicative of

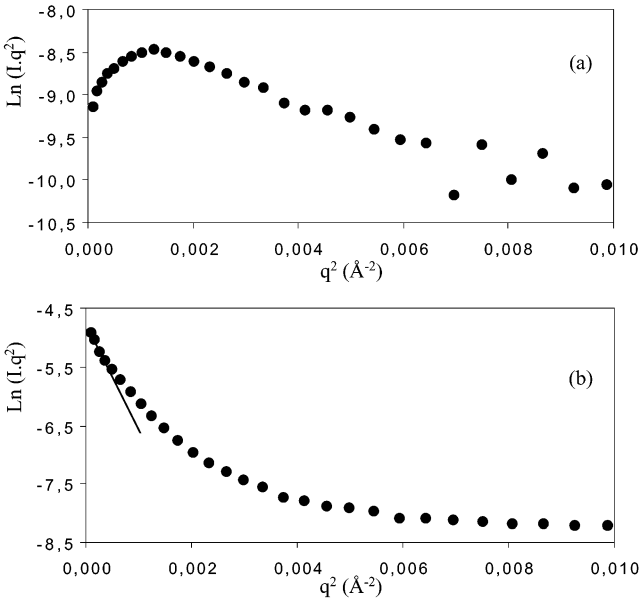


Figure 8. Plot $\ln[Iq^2]$ vs q^2 for copolymer A1 adsorbed on silica from D_2O solutions at concentration: (a) 0.05%; (b) 2%.

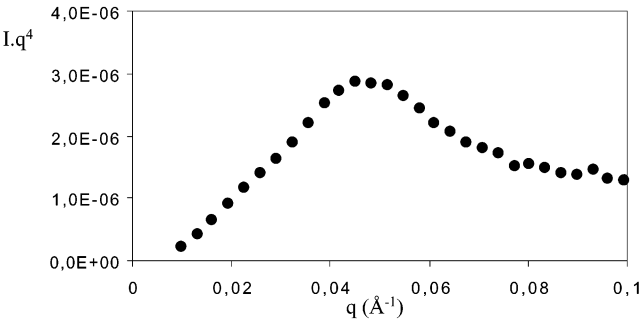


Figure 9. Variation of Iq^4 vs q from D_2O solution of copolymer A3 adsorbed on silica.

Table 6. Adsorption in Water

polymer	% IBVE	M_w (g mol^{-1})	Γ (mg·m^{-2})	h (Å)	R_g (Å)	D (Å)
POXZ 1	0	3150	1.0	65		
A2	20	3780	1.8		31	21
A6	27	2630	4.1	65	24	12
A3	30	1690	5.0	76	20	8
A4	37	1830	5.5	65	13	7
A5	46	3130	7.8	92	21	9
A1	50	5000	7.9	140	26	12

an extended brush structure of the copolymer. As water is a selective solvent for polyoxazoline block, the insoluble block PIBVE spreads on the surface and the soluble block POXZ stretches into the solution like bristles of a brush. The copolymer-adsorbed layer can also be characterized by the grafting density σ and the average distance D between the chains on the surface:

$$\sigma = \frac{\Gamma N_a}{M_w} \tag{7}$$

$$D = 2(\pi\sigma)^{-1/2} \tag{8}$$

where M_w is the molecular weight of the copolymer and N_a the Avogadro number. The high value of the adsorbed amount for copolymer A1 induces a low average distance between the anchoring points of the chains: D = 12 Å. The radius of gyration of the POXZ blocks can

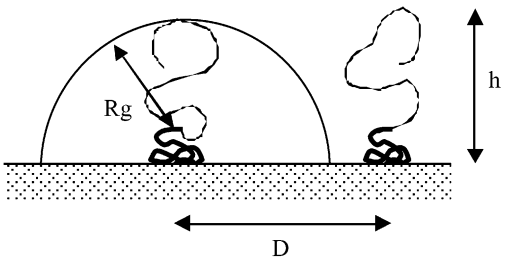


Figure 10. Scheme of copolymer brushes adsorbed on silica from D_2O solution.

be estimated by assuming good solvent conditions ($R_g = a(N_{POXZ})^{0.6}$). The POXZ blocks are clearly interacting in the A1 layer as D is smaller than $R_g = 26$ Å and this should result in a stretched conformation of these blocks (Figure 10). The high value of the apparent thickness of the layer $h = 144$ Å accounts for a highly stretched conformation as the POXZ contour length is on the order of 100 Å.

The influence of the hydrophilic/lipophilic balance has been studied by varying the chemical composition. The results for copolymers containing 0−50% IBVE segments are reported in Table 6. Homopolymer POXZ interact with the silica surface with an adsorbed amount 1 mg/m^2. Copolymer A2 (20% IBVE) adsorbs about two times more than the homopolymer but the scattered intensity plot reveals that the layer is inhomogeneous. For copolymers richer in IBVE (27−50%), the adsorbed layers were denser. Moreover, the low values of D compared to R_g shows that the POXZ layers have the structures of extended brushes. The amount of adsorbed polymer and the thickness of the layer were increased with amount of IBVE incorporated in the copolymer. The thickness of the adsorbed layers have been found to follow qualitatively the theoretical model of Marques and Joanny[5] for the adsorption of diblock copolymers in selective solvents. The grafting densities of the chains are strongly dependent on an asymmetry parameter β in this model:

$$\beta = \frac{a^2 N_{POXZ}^{6/5}}{b^2 N_{PIBVE}} \tag{9}$$

where $a = 3.7$ Å and $b = 2.6$ Å are the segment lengths of OXZ and IBVE, respectively. β is the square of the radius of gyrations'ratio, the POXZ block being assumed in good solvent and the PIBVE block in non solvent. For all the studied samples, β is in the range 10−18 except for copolymer A2 where it is 33. In the regime $\beta \gg 1$, the adsorption results from an equilibrium between the van der Waals interactions in the PIBVE layer and the elastic energy of the POXZ blocks. Minimization of the free energy allows to express the distance D between anchoring points of the chains as a function of N_{POXZ} and β:

$$D = aN_{POXZ}^{3/5}(A/kT)^{-3/23}\beta^{-9/23} \tag{10}$$

A is a Hamaker constant on the order of kT. Experimental D values are plotted in Figure 11 as a function of $(N_{POXZ})^{3/5}\beta^{-9/23}$. A good agreement is obtained with the model, except for A2 where the asymmetry parameter is very large. The PIBVE blocks of A2 are not large enough to ensure an homogeneous anchoring layer, as assumed by the model. It is quite surprising to note that this scaling model, developed for polymers of large

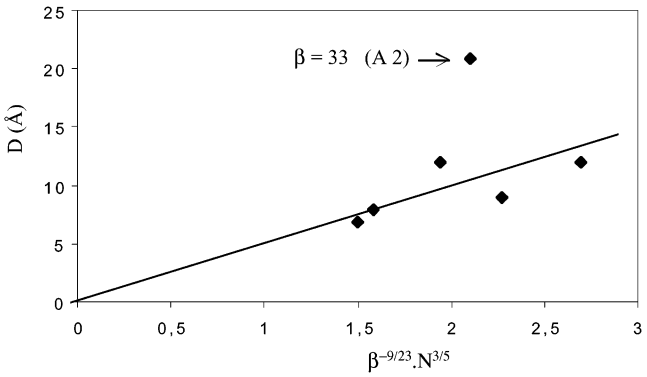


Figure 11. Plot of Marques and Joanny model.

Table 7. Adsorption in Cyclohexane

polymer	% IBVE	Γ (mg·m^{-2})	h (Å)
A3	30	3.6	120
A4	37	3.8	78
A5	46	2.9	70
A1	50	3.0	110
PIBVE 2	100	1.2	46

polymerization degrees, describes quite well the adsorption of the PIBVE-*b*-POXZ copolymers which are made of less than 50 units. Moreover, quite unusually high adsorbed amount have been obtained, the average distance between anchoring points of the chains being as low as 10 Å in some cases. Comparable adsorptions have also been observed for block copolymers poly(dimethylsiloxane)-*co*-poly(ethyloxazoline) under similar conditions.[6] The low molecular weights of the chains probably help to reach the thermodynamic equilibrium of adsorption on a finite time as the kinetic potential barrier to cross for adding chains into the layer is a decreasing function of the molecular weight. We have seen that the POXZ blocks have a non negligible affinity for the silica surface ($\Gamma = 1$ mg/m^2 for homopolymer POXZ). One thus may question the mechanism of adsorption: are the copolymers adsorbing from free polymer chains in equilibrium with the micellar solution, as assumed by the model, or is the adsorbed layer a result of direct adsorption of the micelles sticking to the surface by their POXZ arms? The finding that the model describes well the adsorption gives clues that the first mechanism should occur.

Adsorption in Cyclohexane. Cyclohexane is a selective solvent for the PIBVE blocks. One expects that, at equilibrium, the copolymers will adsorb as diblock monolayers: the insoluble block (POXZ) spreads on the solid surface to form a molten layer, and the soluble block (PIBVE) stretches toward the solution. Adsorption experiments have been performed with copolymers composed of 30% to 50% IBVE units and with homopolymer PIBVE. The results are reported in Table 7. Quite high adsorbed amounts are obtained for the copolymers, 2.9−3.5 mg/m^2, and they are only slightly dependent upon the copolymer compositions. These values are much larger than the homopolymer PIBVE adsorbed amount (1.2 mg/m^2), showing that copolymer−copolymer interactions might take part to the adsorption process. The results of Table 7 show also large thicknesses of the copolymer adsorbed layers which are comparable to the apparent radius of gyration of the micelles (Table 4).

Models of block copolymer adsorption in selective solvent do not give a complete explanation of this

Figure 12. Scheme of copolymer micelles adsorbed on silica from C_6D_{12} solution.

behavior. The asymmetry parameter, from Marques and Joanny model, can be defined in this solvent as

$$\beta = \frac{b^2 N^{6/5}_{\text{PIBVE}}}{a^2 N_{\text{POXZ}}} \tag{11}$$

β values slightly lower than 1 are calculated: from 0.3 (copolymer A3) to 0.9 (copolymer A1). In principle, the Marques and Joanny model is restricted to the domain $\beta \geq 1$. However, due to the scaling nature of eq 11, we assume that the asymmetry parameter are sufficiently close to 1 to use this model. Then the predicted adsorption would be in the buoy dominated regime where the thickness of the molten POXZ layer should be on the order of $a(N_{\text{POXZ}})^{1/2}\beta^{-2}$ (limited to the contour length aN_{POXZ}) and the thickness of the buoy layer (PIBVE) should scale as $b(N_{\text{PIBVE}})^{0.6}$. The total predicted thicknesses are in most cases lower than the experimental ones.

van Lent and Sheutjens[7] have also studied the adsorption of diblock copolymers in selective solvents, in the presence of micellar solution, using self-consistent field theory. For β values lower than 1, they predict high adsorbed amounts (the surface acts as a condensation nucleus for the POXZ block) but they report low extension of the buoy layer in this regime.

Direct adsorption of the micelles on the surface via their PIBVE arms (Figure 12) or formation of more complex structures like multilayers could be alternative explanations of the interfacial behavior in cyclohexane. Liu and colleagues[32] have studied the adsorption of PS-*b*-PCEMA on mica in a mixed solvent of the PS block. Their results show direct adsorption of the micelles via the PS blocks, which then rearrange to form diblock monolayer with PCEMA in contact with mica when the asymmetry parameter is larger than 2. For asymmetry parameter β on the order of 1, they have observed the formation of multilayer on the solid surface.

Conclusions

We have successfully synthesized amphiphilic diblock copolymers PIBVE-*b*-POXZ of varying compositions (containing 20−50% IBVE units). The polymers have been characterized by NMR, SEC, and small-angle neutron scattering. In solution of selective solvents like water or cyclohexane, the copolymers form micellar structures. The adsorption of these copolymers onto porous silica particles has been studied from different nonselective (dichloromethane) or selective (water and cyclohexane) solvents. In a nonselective solvent, dichloromethane, the higher affinity of the surface for the POXZ block drives the adsorption mechanism and the copolymers show a homopolymer type adsorption. Influence of concentration of solutions has been studied in adsorption from aqueous solutions. For dilute watery solutions, the adsorbed chains are in mushroom configuration and the adsorbed amounts are low. On the opposite, stable and very dense copolymer layers corresponding to extended brushes have been obtained in the presence of concentrated watery solutions. The copolymer chains are anchored by the PIBVE blocks which are collapsed on the surface while the POXZ blocks are in a very extended conformation. The influence of the hydrophilic/lipophilic balance has been studied by varying the chemical composition. The amounts of adsorbed polymer are increased with amount of IBVE in the copolymer. The thicknesses of the adsorbed layers have been found to follow qualitatively the theoretical model of Marques and Joanny for the adsorption of diblock copolymers in selective solvents. In cyclohexane, the copolymer compositions of 20−50% IBVE units correspond to longer insoluble blocks than the soluble blocks. Adsorption under these conditions still show dense and thick adsorbed layers which could correspond to direct adsorption of the micelles on the surface.

A rich variety of interfacial architecture can be built from the adsorption of amphiphilic diblock copolymers onto a solid surface: choice of the solvent, block-selective or not selective, and control of the copolymer composition can help to tune the copolymer−solvent interaction and thus influence the adsorption mechanism.

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