Macromolecules **1989**, *22*, 2199–2203 **2199**

Registry No. Polystyrene, 9003-53-6; silica, 7631-86-9; benzene, 71-43-2; acetone, 67-64-1; dioxane, 123-91-1; triethylamine, 121-44-8; pyridine, 110-86-1.

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Random Copolymer Adsorption. 1. Infrared Study at a Silica Surface

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ABSTRACT: Adsorption of styrene–methyl methacrylate (SM) copolymers covering the entire range of chemical composition on a silica surface from trichloroethylene was investigated by using IR and UV spectrometers together with the adsorption of the homopolymers of styrene and methyl methacrylate. Fractionated and well-characterized SM copolymers had mostly similar molecular weights. Adsorbance, the fractions of silanol groups occupied by styrene (θ_s) and by methyl methacrylate units (θ_m), and the fractions of styrene (p_s) and methyl methacrylate units (p_{COH}) that are directly attached to the silanol groups were separately determined. The plateau adsorbance and p_{COH} were dependent on the chemical composition in the SM copolymers. These results were fairly different from the data of Herd et al. (*J. Polym. Sci., Part C* 1971, *34*, 211), and the difference could be interpreted by taking into account the polydispersity effect; that is, large molecules preferentially adsorb over small molecules. The features of SM copolymer adsorption were identified in comparison with the adsorption of ethylene–vinyl acetate as well as that of styrene–butadiene copolymers.

Introduction

There are many copolymer adsorption studies.[1-11] The adsorption behavior of a copolymer at the liquid–solid interface, in general, should be governed by two effects: (1) the solubility of the respective components in a copolymer, i.e., a solvent is a poor solvent for one component and is a good solvent for another component; (2) the interaction strength between components in a copolymer and the surface, i.e., the stronger interaction between a component in the copolymer and the surface than that of another component. For adsorption studies on copolymers of ethylene oxide–propylene oxide[1] in water as well as in benzene and of styrene–butadiene in cyclohexane,[9] the plateau amount adsorbed on the silica surface was dependent on the components in the copolymers, where the results are mainly governed by effect 1. On the other hand, for adsorption studies on copolymers of ethylene–vinyl acetate[2-4,10,11] in various solvents and of styrene–methyl methacrylate[5] in several solvents, the plateau adsorbed amount was independent of chemical composition since vinyl acetate and methyl methacrylate units showed the overwhelming strength of the carbonyl–silanol interaction for the respective adsorption, where effect 2 was dominant.

However, our recent data[11] for the adsorption of fractionated ethylene–vinyl acetate copolymers having different compositions on the silica surface showed a slight but clear composition dependence of the plateau adsorbed amount regardless of the vinyl acetate units only interacting (adsorbing) with the silica surface. This result was clearly different from the previous data[4] and could be induced by using the fractionated ethylene–vinyl acetate copolymers with relatively narrow molecular weight distributions. Thus, the results have shown that one could expect to obtain a much clearer dependence of the plateau adsorbed amount on the component for the adsorption of the styrene–methyl methacrylate (SM) copolymer than for that of the ethylene–vinyl acetate copolymer since both styrene and methyl methacrylate units should interact with the surface. Moreover, the SM copolymer can be easily prepared by radical polymerization in the entire range of components and fractionated to obtain relatively narrow molecular weight distribution samples.

The aim of this paper is to offer experimental data for the adsorption of fractionated SM copolymers onto a

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Table I
Polymerization Conditions of SM Copolymers

sample	styrene dosage, mol %	concn of AIBN, g/dL
SM25	16.6	0.195
SM50	48.5	0.202
SM75	81.6	0.209
SM96	97.4	0.181

Table II
Molecular Characteristics of SM Copolymers

sample	styrene, mol %	$10^{-3}M_n$	M_w/M_n
SM25	25.0	212	1.14
SM50	49.0	197	1.35
SM75	78.7	145	1.27
SM96	96.0	165	1.24

well-characterized Aerosil 130 silica from trichloroethylene solutions at 25 °C as a function of SM copolymer composition. Measurements of the copolymer adsorption were carried out with IR and UV spectrometers as a function of styrene content for the mostly similar molecular weights. The measured values for the adsorbed amount, the fractions of silanol groups on the silica surface occupied by styrene and methyl methacrylate units, and the bound fractions of the styrene and methyl methacrylate units are compared with those for styrene and methyl methacrylate homopolymers. The features of adsorption behavior for the fractionated SM copolymers are discussed by comparison with previous data.[5,9]

Experimental Section

Materials. Four SM copolymers were prepared by free radical polymerization of styrene and methyl methacrylate in the bulk state. The initiator used was AIBN, which was recrystallized twice in ethanol and dried under vacuum. The monomer mixture and a small amount of AIBN were placed in a Pyrex tube, and the contents were thoroughly outgassed by several freeze–degas–thaw cycles before the tube was vacuum sealed. Polymerization temperature was around 70 °C and controlled by thermostated water. The conversion was suppressed to exceed 10%. The details of the polymerization conditions are tabulated in Table I.

The polymer and unreacted monomer mixture was dissolved in benzene and polymer was precipitated by adding the benzene solution into the large amount of methanol. Dissolution (in benzene) and precipitation (in methanol) were repeated three times to purify the copolymers. Precipitated copolymer was dried under vacuum at room temperature to remove traces of methanol.

Copolymers were dissolved in benzene and fractionated into more than seven fractions by the addition of methanol at 25 °C. Fractionated copolymers were precipitated into methanol, dried under vacuum at room temperature and finally freeze-dried from benzene solution.

The number-average molecular weights of the fractionated copolymer were determined by using a Hewlett-Packard 502 high-speed membrane osmometer in toluene at 25 °C. A Sartorius SM 67 N 11539 filter was used as a semipermeable membrane. The polydispersities of the fractionated SM copolymers were determined from GPC measurements using polystyrenes with narrow molecular weight distributions as a standard. The contents of styrene and methyl methacrylate in the copolymers were determined from ^{1}H NMR spectra of a ~10% solution in $CDCl_3$ at room temperature on a Hitachi FT R-600 NMR spectrometer. The molecular characteristics of the SM copolymers used in this study are summarized in Table II.

Polystyrene (PS) of $M_w = 102 \times 10^3$ and $M_w/M_n = 1.02$ was purchased from Tosoh Co.

Poly(methyl methacrylate) (PMMA) purchased from Scientific Polymer Products Co. was dissolved in benzene and fractionated into more than 10 fractions by the addition of methanol. After the fractionated PMMA samples were dried, they were freeze-dried from their benzene solution. Molecular weights of the fractionated PMMA samples were determined from the intrinsic viscosity measurements in benzene at 25 °C by the following relationship between intrinsic viscosity and molecular weight.[12]

$$[\eta] = 5.5 \times 10^{-5} M_w^{0.76} \quad (1)$$

The polydispersities of the fractionated PMMA samples were determined in the same manner as for the SM copolymers by GPC measurements. We chose one fractionated PMMA sample of $M_w = 178 \times 10^3$ and $M_w/M_n = 1.10$ for this adsorption study.

Spectroquality trichloroethylene purchased from Dojin Chemical Co. was used without further purification. Extra-pure grade ethylbenzene and methyl isobutyrate were used without further purification.

The nonporous Aerosil 130 silica (Degussa A. G., West Germany) was used as the adsorbent after being heated at 120 °C under vacuum.[9-11] According to the manufacturer, the average particle diameter is 160 Å, the surface area is 141 m^2/g, and the surface concentration of the silanol group on the silica surface is three per 100 Å^2.

Polymer Adsorption. A 10-mL polymer solution in trichloroethylene with known concentration was mixed with 0.3 g of silica in a stoppered glass centrifugation tube. After equilibration by stirring with a magnetic chip at 25 °C the supernatant solution was separated to sediment the silica by using a Kubota KR-200 B centrifuge. The equilibrium concentration, C_p, in the supernatant solution was determined by using a JASCO FT/IR-3 spectrometer for PMMA and by an Ohtsuka Denshi system 77 UV spectrometer for the SM copolymer and PS after evaporating the solvent, drying the residue, and dissolving it in a definite amount of dioxane.

For determination of the fraction θ of silanol groups occupied by polymer chains the sedimented silica gel was placed in an IR cell made from 4 × 4 cm^2 KBr plates and it was subjected to the IR spectrometer with the reference cell containing trichloroethylene or the supernatant solution.

Determination of the fraction of methyl methacrylate units in the SM copolymers and PMMA which are attached directly to the silanol groups was performed by the method similar to that proposed by Killmann and Bergmann:[13] By introduction of pure PMMA solution with a known concentration into the reference cell for compensation, separation of the bands of the bound and free carbonyl groups in the differential IR spectra of the silica suspensions containing adsorbed and free polymers was carried out.

On the other hand, estimation of the fraction of styrene units attached directly to the silanol groups was carried out by the procedure previously described.[9,10]

Results and Discussion

Adsorbance. As seen in Table II, polymers used here are mostly of similar molecular weights. Adsorption behavior of copolymers could be approximated by taking into account the two effects, 1 and 2, described in the Introduction. The adsorption data of the SM copolymer will be mainly determined by effect 2 rather than effect 1, since trichloroethylene is a good solvent for both PS and PMMA from the Flory–Huggins parameter determined by intrinsic viscosity measurements in trichloroethylene, i.e., $\chi = 0.44$ for PS and 0.45 for PMMA, and the preferential adsorption of PMMA over PS in trichloroethylene solution of PMMA–PS mixtures.[14]

All adsorption isotherms are illustrated in Figure 1. The adsorption isotherms are typical high-affinity types, which consists of an initial steep rise in adsorbance followed by a plateau region where adsorbance is almost constant even with an increase in polymer concentration. Those of fractionated SM copolymers reflect that their adsorption isotherms have a steeper increase in adsorbance at lower concentrations than those observed by Herd et al.[5]

Figure 2 shows that the plateau adsorbance is clearly dependent on styrene content, as we expected. The plateau adsorbances of PMMA and SM copolymers exceed that of PS. The plateau adsorbance for the SM copolymers is approximately constant below 50 mol % styrene content and shows a maximum for the SM75 copolymer.

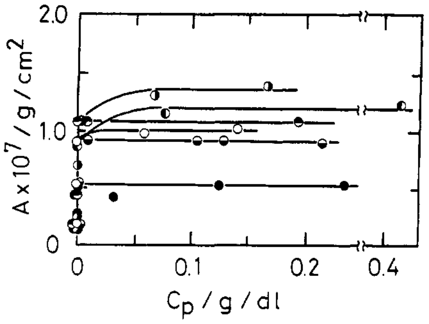

Figure 1. Adsorption isotherms of polystyrene (PS), poly(methyl methacrylate) (PMMA), and SM copolymers: (●) PS; (◒) SM25; (◓) SM50; (◐) SM75; (◑) SM96; (○) PMMA.

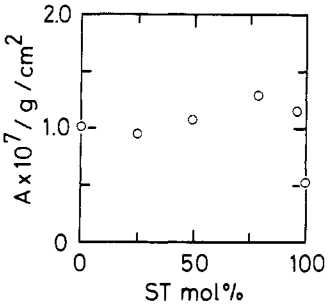

Figure 2. Plateau adsorbed amount of polymers as a function of styrene mole fraction.

This observed result is clearly different from the data of Herd et al.,[5] who have extensively investigated adsorption of MS copolymers on a silica surface in several solvents including trichloroethylene and mainly concluded that the plateau adsorbance stays constant over a wide range of composition. Moreover, their plateau adsorbances are larger than ours for each composition. The difference in the plateau adsorbance may be induced by the polydispersity effect since their samples were not fractionated.

The clear composition dependence of the plateau adsorbance for SM copolymers with above 50 mol % styrene content seems to stem from the fact that both comonomers interact with the silanol groups. This is different from the adsorption of the fractionated ethylene–vinyl acetate copolymer on the silica surface,[11] where vinyl acetate units only interact with the silanol groups. Moreover, this composition dependence is different from that for the adsorption of styrene–butadiene copolymer[9] in cyclohexane, where both units interact with the silanol groups but the solvent is a good solvent for polybutadiene and a poor one for polystyrene. However, at the present time we do not have a reasonable explanation for the existence of a maximum adsorbance at 75 mol % styrene content. Large adsorbance may be explained as a result of the fact that most styrene units protrude into the bulk solution and most methyl methacrylate units are attached to the silica surface. Therefore, SM copolymers with higher styrene contents are expected to form larger loops.

Throughout this paper, it is implicit that all adsorption sites are silanol groups and that no adsorption takes place elsewhere. It is clear that this assumption is valid by referring to the papers of Thies[15] and Dietz.[16] These papers address that the effect of surface modification of the adsorbent on adsorption. It was found that silylation of the silanol groups on the silica surface reduces adsorbance and no adsorption occurs on the fully silylation surface.

Surface Coverage of Silanol Groups. The typical differential infrared spectra between the supernatant solution and the silica gel on which polymers are adsorbed are displayed in Figure 3: (A) silica in trichloroethylene; (B) silica on which PS is adsorbed; (C) silica on which PMMA is adsorbed; (D) silica on which SM50 copolymer is adsorbed. For spectrum D there are three absorption peaks: a band located at 3675 cm^{-1} due to the isolated silanol groups, a band at 3592 cm^{-1} due to the interaction between the silanol groups and the phenyl groups of styrene units in the copolymer, which agrees with the absorption peak of silica immersed in ethylbenzene, an analogous compound to a styrene monomer, and a band at 3433 cm^{-1} due to the interaction between the silanol groups and the carbonyl groups of methyl methacrylate units in the copolymer, and is consistent with the absorption peak of silica immersed in methyl isobutyrate, an analogous compound to a methyl methacrylate monomer. The positions for their absorption peaks coincide with those in the spectra A, B, and C.

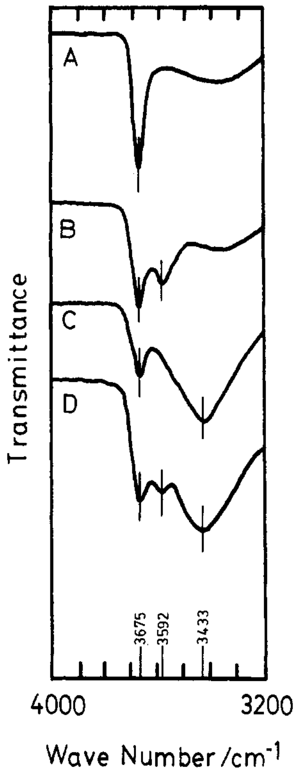

Figure 3. IR differential spectra of sedimanted silica. (A) Silica in trichloroethylene; (B) silica on which PS adsorbs; (C) silica on which PMMA adsorbs; (D) silica on which the MS50 copolymer adsorbs.

The fraction of the silanol groups occupied by adsorbed chains can be calculated by using the same procedure as described previously.[9,10]

The fraction of silanol groups occupied by styrene units, θ_s, and that by methyl methacrylate units, θ_m, can be obtained from the following equations

$$\theta_s = S_{3592}/(S_{3675} + S_{3592} + S_{3433}) \tag{2}$$

and

$$\theta_m = S_{3433}/(S_{3675} + S_{3592} + S_{3433}) \tag{3}$$

where S_{3675}, S_{3592}, and S_{3433} correspond to the number of the free silanol groups, that of the silanol groups occupied by phenyl groups, and that of the silanol groups occupied by carbonyl groups, respectively.

For the calculation we have to know the extinction coefficients ϵ for the respective absorption peaks: ϵ_{3675} = 74.1 L mol^{-1} cm^{-1}, as determined from the silica immersed in trichloroethylene, ϵ_{3592} = 148 L mol^{-1} cm^{-1} in ethylbenzene, and ϵ_{3433} = 111 L mol^{-1} cm^{-1} in methyl isobutyrate.

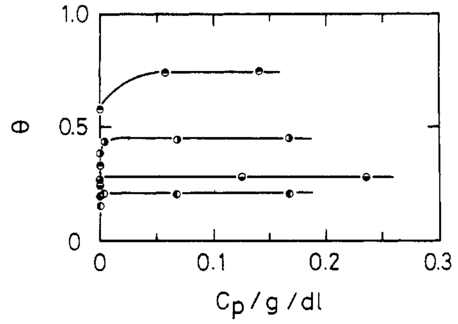

Figure 4. Plots of the fraction θ of silanol groups occupied by polymers versus the equilibrium polymer concentration C_p. (◒) PS; (◓) PMMA; (◐) fraction of silanol groups occupied by styrene units in the SM75 copolymer; (◑) fraction of silanol groups occupied by methyl methacrylate units in the SM75 copolymer.

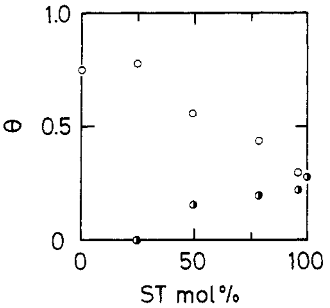

Figure 5. Plateau fractions of silanol groups occupied by styrene (◑) and by methyl methacrylate units (○) as a function of styrene mole fraction.

Figure 4 shows, typical plots of the surface coverage of the silanol groups versus the equilibrium concentration in the supernatant solution for PS, PMMA, and the SM75 copolymer. For the SM75 copolymer the fractions of silanol groups occupied by styrene (θ_s) and by methyl methacryrate units (θ_m) are separately plotted in the figure. Irrespective of the polymer species, the surface coverage shows a steep rise at a low polymer concentration and reaches a plateau value above C_p = 0.1 g/100 mL.

The plateau θ_s and θ_m values are plotted versus styrene contents together with the plateau θ value for the styrene and methyl methacrylate homopolymers in Figure 5. The plateau θ_m decreases with an increase in styrene contents; in contrast, the plateau θ_s increases. Particularly, for the SM25 copolymer, the θ_s value being zero is attributed to the weak interaction between the phenyl group and silanol group. The total fraction, θ_t, of the silanol groups occupied by the copolymers is defined by the sum of θ_s and θ_m, which decreases with an increasing styrene content and generally does not exceed the surface coverage for PMMA as seen in Table III except for the SM25 copolymer.

Bound Fraction of Monomer Units. The fraction, p_s, of styrene units directly attached to the silica surface was determined from the following equation[17] by assuming that one phenyl group should interact with one silanol group, since it was difficult to separate the bands of bound and free phenyl groups in the differential IR spectra between the silica suspensions containing adsorbed PS and no polymer due to the small difference in the absorption frequency between bound and free phenyl groups ($\Delta\nu$ = 4 cm^{-1}). For PS

$$p_s = \text{[wt of attached styrene units on silanol groups]/[wt of adsorbed amount (adsorbance)]} \quad (4)$$

For the copolymer

$$p_s = \text{(wt of attached styrene units on silica groups)/(wt of total adsorbed styrene units)} \quad (5)$$

Table III
Plateau Adsorption Data of SM Copolymers, PMMA and PS

sample	adsorbance × 10^8, g/cm^2	θ_s	θ_m	p_s	p_{COH}	p_{tot}
PMMA	10.3	0	0.75	0	0.18	0.18
SM25	9.1	0	0.78	0	0.35	0.26
SM50	10.8	0.17	0.57	0.19	0.34	0.27
SM75	14.1	0.21	0.45	0.20	0.44	0.25
SM96	12.4	0.23	0.38	0.20	1.0	0.23
PS	5.4	0.28	0	0.24	0	0.24

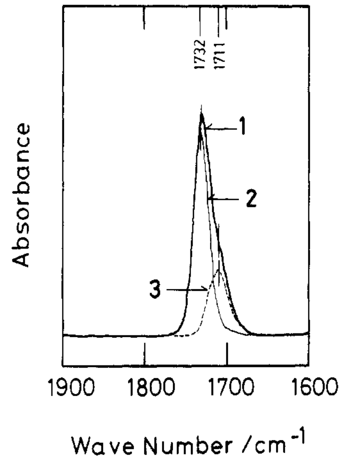

Figure 6. IR spectra: (1) PMMA in trichloroethylene/Aerosil suspension; (2) PMMA in trichloroethylene solution; (3) compensated spectrum.

The numerators in eq 4 and 5 are obtained from the product of the number of silanol groups occupied by the phenyl group and the molecular weight of a styrene unit. The denominator in eq 5 corresponds to the product of the adsorbed amount and the weight fraction of styrene units in the copolymer.

On the other hand, for carbonyl groups in PMMA and SM copolymers the difference in the absorption frequency between bound and free carbonyl groups has a fairly larger value of $\Delta\nu$ = 21 cm^{-1} than that for a phenyl group. A typical differential IR absorption band of the bound and free carbonyl group between silica suspensions containing PMMA chains and no polymer is shown in Figure 6 together with an IR spectrum (2) of PMMA in trichloroethylene solution and the compensated spectrum (3) of the band of the adsorbed carbonyl groups of PMMA. According to the method of Killmann and Bergmann,[13] the concentration of the bound carbonyl group C_{COH} is correlated with the concentrations of dosage polymer (C_o) and pure polymer solution in the reference (C_c).

$$C_{COH} = C_o - d_c C_c / d \quad (6)$$

where d and d_c are path length of the cell filled with silica suspension and that of the cell with polymer solution in the reference, respectively. Provided that d_c is adjusted to equal d, the value C_{COH} is a difference between C_o and C_c. This condition is satisfied in our experiments. The fraction, p_{COH}, of attached carbonyl groups is defined as

$$p_{COH} = C_{COH} / C_A \quad (7)$$

where C_A corresponds to $C_o - C_p$.

In Figure 7, typical plots of the fraction of monomer units attached to the silica surface versus C_p are illustrated for PS, PMMA, and the SM50 copolymer. The fraction of attached monomer units has a large value at low C_p and reaches a plateau value above C_p = 0.1 g/100 mL, irrespective of polymer species. A similar concentration de-

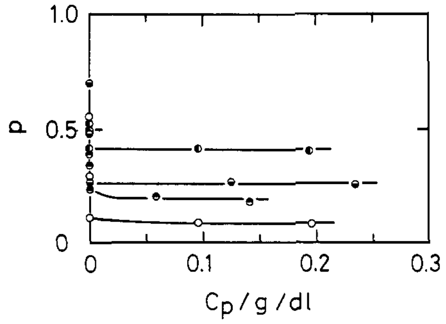

Figure 7. Plots of the fractions *p* of styrene and methyl methacrylate units directly attached to the silica surface versus the equilibrium polymer concentration C_p. (◒) PS; (◓) PMMA; (○) fraction of styrene units in the SM50 copolymer; (◐) fraction of methyl methacrylate units in the SM50 copolymer.

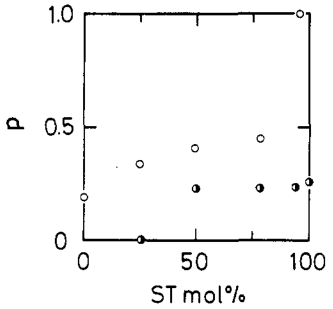

Figure 8. Plateau bound fractions of styrene (◑) and methyl methacrylate (○) units as a function of styrene mole fraction.

pendence is observed for other SM copolymers. The plateau values of the fraction of attached monomer units are summarized in Table III.

The plateau values in Table III are plotted versus styrene contents in Figure 8. The fraction of attached styrene units is approximately independent of the styrene content, while the fraction of attached methyl methacrylate units increases with increasing styrene contents. These results are in qualitative agreement with the data of Herd et al.[5] For the SM97 copolymer, the unity of the p_{COH} value is possible to establish by taking into account the strong interaction between the carbonyl group and silanol group as well as the small contents of methyl methacrylate units in the copolymer.

Total fraction p_{tot} of adsorbed SM copolymers can be calculated from both values of p_s and p_{COH}

$$p_{tot} = w_s p_s + (1 - w_s) p_{COH} \qquad (8)$$

where w_s is the weight fraction of styrene units in the SM copolymers. The plateau values of p_{tot} so calculated are summarized in Table III. The plateau value of p_{tot} is approximately independent of styrene content in the entire range. This result is quite different from that for the adsorption of the styrene–butadiene (SB) copolymer[9] onto the silica surface where the plateau p_{tot} increases with increasing styrene contents. This difference is attributed to the fact that adsorption behavior of SM copolymers is mainly governed by effect 2, while for adsorption of the SB copolymers, effect 1 is dominant.

Conclusions

Use of fractionated styrene–methyl methacrylate copolymers having relatively narrow molecular weight distributions and mostly similar molecular weight clarifies the features for the adsorption behavior of a random copolymer in comparison with the homopolymers of styrene and methyl methacrylate by the measurements of adsorbance, the surface coverage of silanol groups occupied by the respective monomer units, and the fraction of respective monomer units directly attached to the silica surface. Particularly, the clearer composition dependence of adsorbance than the old data of Herd et al.[5] can not be interpreted without consideration of the preferential adsorption of large molecules over small molecules.

Registry No. PS, 9003-53-6; PMMA, 9011-14-7; SM (copolymer), 25034-86-0; Aerosil 130 silica, 7631-86-9.

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