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Random Copolymer Adsorption. 2. Competitive and Displacement Adsorption

Masami Kawaguchi,* Katsunori Itoh, Satoshi Yamagiwa, and Akira Takahashi

Department of Industrial Chemistry, Faculty of Engineering, Mie University, 1515 Kamihama-cho, Tsu, Mie 514, Japan. *Received June 6, 1988; Revised Manuscript Received October 12, 1988*

ABSTRACT: Competitive and displacement adsorption of polystyrene (PS) and poly(methyl methacrylate) (PMMA) or styrene–methyl methacrylate (SM) copolymer having a wide range of styrene contents onto a nonporous Aerosil 130 silica from trichloroethylene solutions at 25 °C was investigated by using a FT-IR spectrometer. In competitive adsorption, PMMA and SM copolymer chains adsorb preferentially over PS chain, and for PS–SM copolymer mixtures, the preferential adsorption of a higher styrene content SM copolymer over a lower one was observed even in the presence of PS chains. In displacement adsorption, PMMA chains completely exchange PS chains and the higher styrene content SM copolymers replace many more PS chains than lower styrene content ones. The competitive and displacement adsorption behavior of PS and SM copolymers could be correlated with the plateau adsorbed amount for individual adsorption of SM copolymers.

Introduction

Several studies on the competitive and displacement adsorption of homopolymers with different chemical structures onto the solid surfaces have been performed and have led to common and significant conclusions:[1-5] (1) In competitive adsorption, the polar polymer molecules preferentially adsorb to the surface. (2) In displacement adsorption more polar polymer chains replace less polar ones, larger displacer chains have a greater exchangeability, and larger polymer chains are not easily desorbed from the surface. In contrast, there has been a some research[6,7] focusing on the competitive and displacement adsorption of homopolymers and copolymers; Botham and Thies[6] reported that polystyrene and ethylcellulose were desorbed by the ethylene–vinyl acetate (EVA) copolymer and that EVA copolymers with higher vinyl acetate content replaced those with lower content. The same authors[7] described that polystyrene was preferred to polybutadiene and to di- and triblock styrene–butadiene copolymers. However, comprehensive data of the competitive and displacement adsorption of homopolymers and random copolymers as functions of chemical composition in the copolymer and dosage have been lacking.

In a preceding paper[8] the individual adsorption of fractionated styrene–methyl methacrylate (SM) copolymers onto a nonporous silica (Aerosil 130) from trichloroethylene solutions has been extensively investigated by using an IR spectrometer and a UV spectrometer. Its adsorption behavior has been clarified as a function of styrene content in terms of the adsorbed amount, the fractions of the silanol groups occupied by styrene and by methyl methacrylate units, and the fractions of styrene and methyl methacrylate units directly attached to the surface. Thus, we would expect that the competitive and displacement adsorption of SM copolymers and the styrene homopolymer seems to be characterized by styrene content, since methyl methacrylate units should be preferred to styrene units.[1]

The aim of this paper is to present experimental results for the competitive and displacement adsorption of styrene and methyl methacrylate homopolymers, including their random copolymers, onto a nonporous Aerosil 130 silica from trichloroethylene solutions at 25 °C. Each sample has a relatively narrow molecular weight distribution. Measurements were carried out by using an FT–IR spectrometer. The characteristics of the competitive and displacement adsorption of the SM copolymer are discussed in terms of adsorbed amounts by comparison with that for styrene and methyl methacrylate homopolymers.

Table I
Characteristics of Polymer Samples

sample	mol wt × 10^{-3}	M_w/M_n	styrene fractn, mol %
PMMA-1	595[a]	1.09	0
PMMA-2	40.3[a]	1.20	0
SM25	252[b]	1.15	25.0
SM50	167[b]	1.31	49.3
SM75	131[b]	1.23	78.7
PS	775[a]	1.01	100

[a] Weight-average molecular weight. [b] Number-average molecular weight.

Experimental Section

Materials. SM copolymers were prepared from free radical polymerization of styrene and methyl methacrylate in the bulk state with a small amount of AIBN as described in a preceding paper.[8] They were fractionated into more than 10 fractions in benzene by the addition of methanol. Molecular characterization of the fractionated SM copolymers was performed by a procedure previously described and the characteristics of the SM copolymers used here are summarized in Table I.

Poly(methyl methacrylate) (PMMA) purchased from Scientific Polymer Products Inc. was fractionated in a benzene/methanol system at 25 °C as described in a previous paper.[8]

Polystyrene (PS) of $M_w = 775 \times 10^3$ and $M_w/M_n = 1.04$ was purchased from Tosoh Co.

Nonporous Aerosil 130 silica (Degussa AG., West Germany) was used as the adsorbent and cleaned at 120 °C under vacuum before use.[9] According to the manufacturer, the particle diameter is 160 Å, the surface area is 141 m^2/g, and there are three silanol groups per 100 $Å^2$.

Spectroquality trichloroethylene purchased from Dojin Chemical Co. was used as a solvent without further purification.

Individual and Competitive Adsorption. Twenty milliliters of polymer solution containing a known concentration was mixed with the cleaned silica (0.16 g) in a stoppered glass centrifugation tube. The mixture was placed in an incubator controlled at 25 ± 0.1 °C and agitated by a magnetic stirrer chip for the desired periods of time, usually 24 h. After equilibration the silica was sedimented by a Kubota KR-200B centrifuger. The equilibrium concentrations, C_p, in the supernatant solutions were determined by using a Nihon Bunko FT/IR-3 spectrometer and an Ohtsuka Denshi System 77 UV spectrometer.

For the competitive adsorption studies the two polymers in PMMA–PS and SM copolymer–PS mixtures were premixed in trichloroethylene at the desired concentration (1:1 (wt/wt)) C_0 and a 20 mL of mixture in trichloroethylene was mixed with Aerosil 130 silica (0.16 g) in a stoppered glass centrifugation tube

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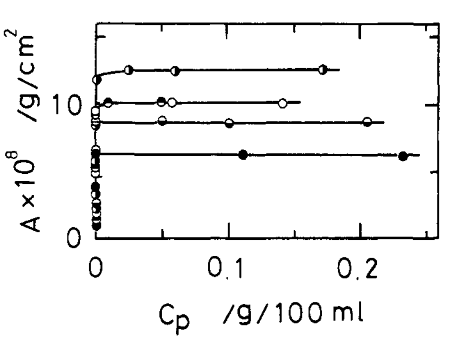

Figure 1. Adsorption isotherms of PS, PMMA, and SM copolymers onto Aerosil 130 silica from trichloroethylene solution at 25 °C: (●) PS; (◑) SM75; (⊖) SM50; (⊝) SM25; (○) PMMA-2.

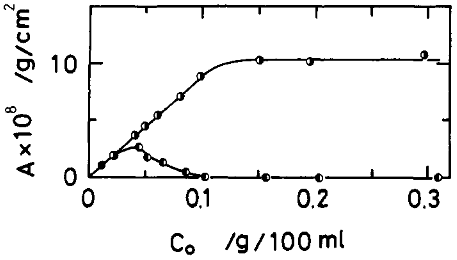

Figure 2. Competitive adsorption isotherms of a PS and PMMA-1 mixture. C_0 is the dosage concentration of each polymer: (◐) PS; (◑) PMMA-1.

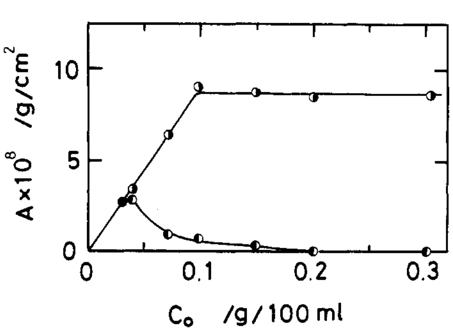

Figure 3. Competitive adsorption isotherms of a PS and SM25 copolymer mixture. C_0 is the dosage concentration of each polymer: (◐) PS; (◑) SM25 copolymer.

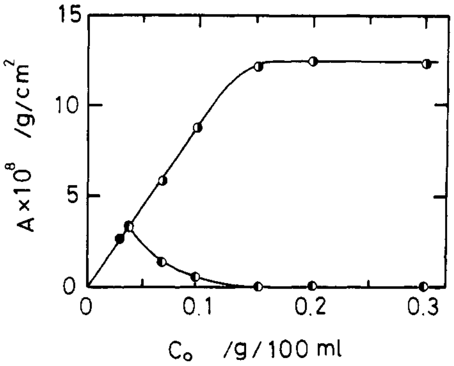

Figure 4. Competitive adsorption isotherms of a PS and SM75 copolymer mixture. C_0 is the dosage concentration of each polymer: (◐) PS; (◑) SM75 copolymer.

and conditioned at 25 °C for 24 h in the incubator. After sedimenting the silica the equilibrium concentrations, C_p, of two polymers in the supernatant solutions were determined by using the FT-IR spectrometer.

Displacement Adsorption. PS molecules were adsorbed onto the silica (0.16 g) from 20 mL of trichloroethylene solution containing 0.1 g/100 mL, a concentration well in the plateau region for the adsorption isotherm of the individual adsorption.[8] After equilibration of PS with the silica, subjecting of the silica to sediment, and withdrawing of 10 mL of the supernatant solutions, 10 mL of SM copolymer (or PMMA) trichloroethylene solution at the desired concentration was added to the system. The mixture was conditioned and centrifuged to sediment the silica. The concentrations of the PS and SM copolymer (or PMMA) in the supernatant solutions were determined by the same procedure as employed in the competitive adsorption studies.

Results and Discussion

Individual Adsorption. Adsorption isotherms of individual polymers are of the high affinity type as shown in Figure 1, reflecting the narrow molecular weight distribution. The plateau adsorbed amount of SM copolymers depends on the methyl methacrylate contents and increases in the order of SM75, SM50, and SM25. The magnitude of the plateau adsorbed amounts for the respective SM copolymers is approximately the same as that for the previous study,[8] regardless of the different molecular weights of the SM copolymers.

Competitive Adsorption. Figure 2 shows a competitive adsorption isotherm, i.e., a plot of adsorbed amounts of PS and PMMA-1 of M_w = 595 × 10^3 against the initial added concentration C_0 of PS (or PMMA). Both polymer molecules adsorb completely onto the silica surface below C_0 = 0.02 g/100 mL. Above this concentration all PMMA molecules adsorb up to C_0 = 0.1 g/100 mL and the adsorbed amount attains a constant value, which is equal to the plateau adsorbed amount for the adsorption isotherm of PMMA-1. In contrast, the remaining amount of PS molecules in the supernatant solution increases with increasing C_0 and no PS molecules adsorb onto the silica above C_0 = 0.1 g/100 mL. Other PS–PMMA mixtures[10] indicate a similar trend. Therefore, PMMA chains preferentially adsorb over PS ones. This result is in good agreement with the data of Thies.[1]

Figures 3 and 4 show the competitive adsorption isotherms of the PS–SM25 copolymer and PS–SM75 copolymer mixtures, respectively. Below C_0 = 0.03 g/100 mL both PS and MS copolymer molecules completely adsorb onto the silica surface, a preferential adsorption of MS copolymer over PS molecules is more clearly observed with an increase in C_0, and finally adsorbed amounts of both polymers in the mixtures reach a constant value.

Close inspection shows a significant difference in the competitive adsorption between the PS–SM25 copolymer and the PS–SM75 copolymer mixtures. The lowest C_0 where the adsorbed amount of SM copolymer reaches a constant value is different in each case, i.e., C_0 = 0.1 g/100 mL for PS–SM25 mixture and C_0 = 0.15 g/100 mL for PS–SM75 mixture, and the adsorbed amounts of SM copolymers at the corresponding concentration coincide with the plateau adsorbed amounts for the individual adsorption of SM copolymers. For the PS–SM75 copolymer mixture at C_0 = 0.15 g/100 mL, no PS molecules adsorb on the silica surface and above C_0 = 0.15 g/100 mL a complete preferential adsorption of the SM75 copolymer over PS is observed. In contrast, for the PS–SM25 copolymer mixture some PS molecules still can adsorb onto the silica surface even if C_0 = 0.15 g/100 mL.

Preferential adsorption phenomena for PS–PMMA and PS–SM copolymer mixtures could be explained by taking into account the difference between the styrene–silanol and methyl methacrylate–silanol interactions. Such an interaction, corresponding to a measure of the adsorption strength of monomer units and silanol groups, could be related to the infrared absorption shift of the silanol group.[11-13] The frequency shifts, $\Delta\nu_{OH}$, of silanol groups due to adsorption of PS and PMMA were 83 and 242 cm^{-1}, respectively.[8] This means that methyl methacrylate units adsorb more tightly onto the silica surface than styrene units.

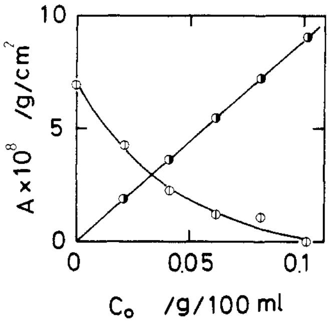

Figure 5. Adsorbed amounts for displacement adsorption of PS by PMMA-2 as a function of concentration of PMMA-2: (⦶) PS; (◑) PMMA-2.

However, the difference in the preferential adsorption between the PS–SM25 copolymer and PS–SM75 copolymer mixtures above C_0 = 0.15 g/100 mL cannot be fully interpreted by the difference in surface–polymer segment interactions, because the SM25 copolymer contains larger methyl methacrylate units than the SM75 copolymer. We noticed two important facts concerning the competitive adsorption of the PS–SM copolymer mixtures: First, the preferential adsorption of large polymers over small polymers in the presence of other chemically different polymers is not realized in the mixtures of PS and SM copolymers, since the small SM75 copolymer has a stronger preferential adsorbability lity for PS than the larger SM25 copolymer. Second, the difference in the magnitude of the adsorbed amounts between SM copolymers above C_0 = 0.15 g/100 mL, corresponding to the difference in the plateau adsorbed amount for the individual adsorption, could be correlated with the difference in the competitive adsorption between the PS–SM75 copolymer and PS–SM25 copolymer mixtures.

Displacement Adsorption. From the preferential adsorption of PMMA molecules over PS molecules it is expected that PMMA molecules replace PS molecules. Figure 5 shows a displacement adsorption isotherm of PS molecules, which are first fully adsorbed onto the silica surface and replaced by the addition of PMMA-2 having a M_w = 40.3 × 10^3. The initial concentrations, C_0, of PMMA-2, ranging from 0.02 to 0.1 g/100 mL, are lower than the concentration at which the plateau adsorbed amount of PMMA-2 is attained for its individual adsorption. As C_0 is increased the degree of displacement of PS molecules by PMMA molecules proceeds, while all PMMA-2 molecules adsorb onto the silica surface. At C_0 = 0.1 g/100 mL PS molecules are completely desorbed from the silica surface. Other combinations of PS–PMMA[10] show that the initial concentration of PMMA, where the complete displacement of PS has taken place, is lower when the PMMA chains are larger and PS chains are smaller. This molecular weight dependence on the displacement adsorption of PS by PMMA is in agreement with that for the displacement adsorption of PS by PEO.[4]

For the displacement of PS molecules by SM copolymers we intutively imagine that the SM25 copolymer should own the strongest desorbability for PS molecules since it has the largest methyl methacrylate content among three SM copolymers. Figures 6, 7, and 8 show the displacement adsorption isotherms of PS molecules preadsorbed in the plateau region for the PS adsorption isotherm by the addition of SM25, SM50, and SM75 copolymers, respectively. The initial concentrations, C_0, of the SM copolymers range from 0.02 to 0.15 g/100 mL.

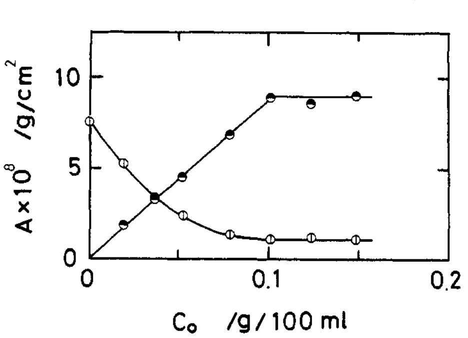

Figure 6. Adsorbed amounts for displacement adsorption of PS by SM25 copolymer as a function of concentration for SM25 copolymer: (⦶) PS; (◒) SM25 copolymer.

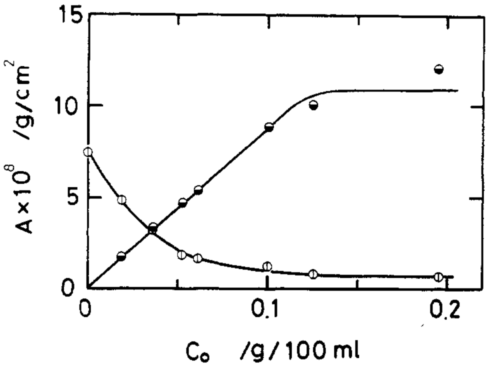

Figure 7. Adsorbed amounts for displacement adsorption of PS by SM50 copolymer as a function of concentration for SM50 copolymer: (⦶) PS; (◒) SM50 copolymer.

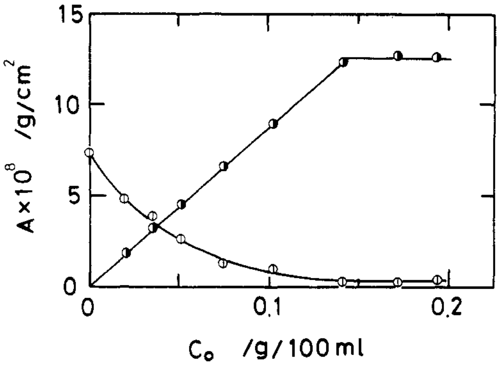

Figure 8. Adsorbed amounts for displacement adsorption of PS by SM75 copolymer as a function of concentration for SM75 copolymer: (⦶) PS; (◑) SM75 copolymer.

We should notice some remarkable differences among the displacement adsorption isotherms. For all displacement adsorption isotherms the remaining amount of the preadsorbed PS molecules rather steeply decreases at lower C_0's of the SM copolymers, gradually decreases with increasing C_0, and then finally reaches a constant value. The lowest C_0 at which the remaining amount of the preadsorbed PS attains a constant value depends on the SM copolymers and is approximately consistent with the concentration where the adsorbed amount reaches the plateau value in the individual adsorption. Therefore, the plateau adsorbed amounts in the adsorption isotherms for individual adsorption of the SM copolymers seem to be also correlated with the displacement of PS by the SM copolymer. The degree of displacement for the preadsorbed PS is almost the same value (~0.75) for the SM25 and SM50 copolymers, while the SM75 copolymer replaces more PS molecules at the silica surface than the two SM copolymers. Therefore, this result is inconsistent with our expectation as previously described.

For interpretation of the displacement adsorption of the preadsorbed polymer chains by displacer polymer molecules, in general, we should take into account several factors, such as (1) the interaction between polymer segment and surface, (2) the fraction of polymer segments directly attached to the surface, (3) the concentration of displacer, and (4) the molecular sizes of the preadsorbed polymer and displacer. We can ignore factor 2 because of the constant total fraction of adsorbed SM copolymer segments in the entire range studied, as described in the previous paper.[8] Also, we need not take into account the molecular size of a preadsorbed polymer chain since we use only one molecular weight for PS.

The displacement of PS by PMMA[1,2] as well as by PEO[4] strongly depended on the size of a displacer polymer chain. Namely, a large chain of a displacer molecule could completely replace the preadsorbed chain at the lower concentration in comparison with a small displacer polymer. In this experiment, however, the result of displacement adsorption shows the reverse tendency; i.e., the smallest SM75 copolymer chain behaves as the best displacer.

Of course, factor 1, corresponding to the difference in surface–polymer segment interaction strength between methyl methacrylate–silanol and styrene–silanol, should be dominant for the displacement adsorption. Since the concentration of the SM copolymer giving the constant remaining amount of PS molecules preadsorbed agrees with that giving the plateau adsorbed amount of SM copolymer for individual adsorption, factor 3 is also attributed to the displacement adsorption of PS by the SM copolymer.

Conclusions

Competitive and displacement adsorption of PS by SM copolymers onto the silica surface exhibits some markedly different behaviors from that of different chemical homopolymers. SM copolymers preferentially adsorb and replace PS. A SM copolymer higher in styrene content shows a better preferential adsorption and behaves as a better displacer, regardless of the smaller chain. The preferential adsorption behavior of SM copolymer over PS chains is well correlated with the magnitude of the plateau adsorbed amounts in the adsorption isotherms for the individual adsorption of the SM copolymers.

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

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Trap-Site Formation and Trap-Controlled Triplet Energy Migration in Phenanthrene Copolymer Films

Shinzaburo Ito, Norio Numata, Hideaki Katayama, and Masahide Yamamoto*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.
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ABSTRACT: Triplet spectroscopy and energy migration among phenanthrene chromophores in poly[(9-phenanthrylmethyl methacrylate)-*co*-(methyl methacrylate)] film were investigated. The copolymerization of a chromophoric monomer with a photophysically inert monomer provides a polymer system having high chromophore concentrations in a uniform distribution. At temperatures below 150 K, the phenanthryl moieties did not form a deep trap such as a triplet excimer, but they formed a shallow trap with diverse energy levels which were reflected in the phosphorescence spectra as red shifts which depended on the concentration of the chromophore and on the film temperature. The energy migration process was observed by the rise of sensitized emission from a triplet energy acceptor, 1,4-dibromonaphthalene, after pulsed excitation of a phenanthrene chromophore. The average rise time showed a marked temperature dependence. This indicates that the migration occurs with iterative trapping–detrapping processes at the trap sites and is enhanced by thermal activation. This system gives a typical example of trap-controlled photophysics of the triplet state.

Introduction

Electronically excited states of polymers with pendant aromatic chromophores have been widely investigated.[1] Most of the work in this field has been carried out on the singlet state, because fluorescence is usually intense and easily detectable by steady-state and time-resolved spectroscopic techniques. However, the triplet state has not been studied as much as the singlet state, owing to some experimental difficulties, although it is important from the fundamental as well as application standpoints. A large portion of the excitation energy, often exceeding 50%, dissipates to the ground state via the triplet state. In connection with photofunctional materials, the polymer solid is an important system and its photophysical processes should be clarified in detail. Many photochemical reactions involving triplet states have been utilized for so-called photosensitive polymers, and "triplet sensitizers" are often used. However, in many cases the primary processes have not been fully understood, because of experimental difficulties such as weak emission due to efficient nonradiative deactivation.

In condensed phases such as polymer matrices, excited chromophores are often involved in various interchromophoric processes, including energy migration and excimer

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