

Synthesis and Behavior of the Polymer Covering on a Solid Surface. II. Effect of the Adsorbent Particle Size on Adsorption

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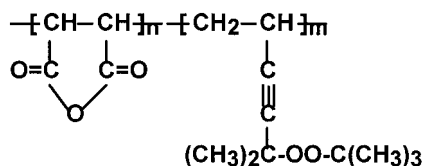
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ABSTRACT: Adsorption of poly(5-*tert*-butylperoxy-5-methyl-1-hexen-3-yne-*co*-maleic anhydride) and poly(styrene-*co*-maleic anhydride) on the various ultrafine powders (TiO₂, ZnO, Al₂O₃, CaCO₃, aerosil, and quartz powder) was studied. Plateau adsorption amount per unit surface of adsorbent (α^s) decreased with the decreasing of particle size of the adsorbent. The α^s -molecular mass relationship was different for copolymers of low and high molecular mass. The fractal dimension $D = 2.5$ of adsorbent surface was determined if the particle radius was less than 2.5 μm . Fractal behavior was explained by aggregation of particles. Due to the aggregation the interparticle space (pore) in the area of contact of neighboring particles is inaccessible for the polymer and accessible for the solvent. The experimental isotherm with maximum was employed for estimation of the volume of inaccessible pores 2.4 cm³/g for suspension of aerosil.
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Key words: polymer adsorption; fractal dimension; aggregation

INTRODUCTION

In our recent article¹ we discussed the adsorption of reactive copolymer (PM–MA) of peroxide monomer (PM) 5-*tert*-butylperoxy-5-methyl-1-hexen-3-yne and maleic anhydride (50 : 50 % mol)²:



on the solid–liquid interface.

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It was found that physisorption of PM–MA on a solid surface is a suitable way to attach the initiator of radical graft polymerization. The effect of solvent, adsorbate nature, and temperature was studied. In this article we report the adsorption on adsorbent particles of various size. This topic seems to be important because a wide range of particle size (0.01–100 μm) is used in various applications. On the other hand, ultrafine powders with high specific surface are usually used as model materials for studying of characteristic features of the adsorption or grafting process. Uniformity of polymer covering and accurate evaluation of the amount of the adsorbed or grafted chains is the basis for many theoretical considerations and practical applications.

All general points of polymer adsorption theory now discussed in the literature³ are based on the experiments and models developed for infinitely

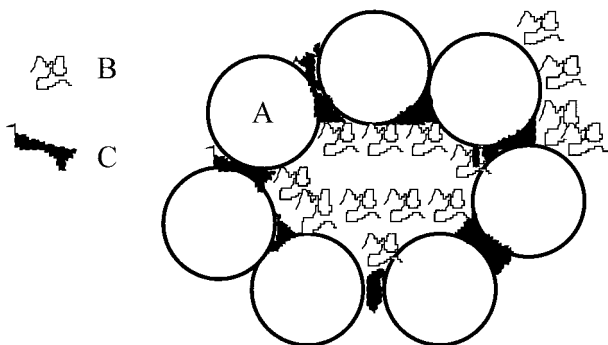


Figure 1 Schematic illustration of inaccessible pores (C) in the aggregate of adsorbent particles (A) with adsorbed polymer chains (B).

extended flat surfaces even if the experiments were done for colloidal adsorbents due to the presumption that the radius of surface curvature was well beyond the radius of gyration of the polymer coil in solution. Nevertheless, a few reported studies^{4–15} showed considerable effect of the ratio of coil and colloidal particle sizes on adsorption. In those works the most attention is dedicated to the limiting case when the size of the polymer coil considerably exceeds the radius of adsorbent particle. In this case, each macromolecule may cover many particles simultaneously. However, the intermediate case when the particle size is about 10–100 times higher than the size of the macromolecule was not analyzed in detail, despite of the wide range of applications of the systems with such ratio. Such particles form aggregates that may not be destroyed in the dispersion medium. The space between individual particles in the aggregate near the “point” of the particles “contact” may be considered as a pore (Fig. 1). The size of such a pore could be close to the size of the macromolecular coil. The latter means a possible restriction in polymer adsorption or at least change in adsorbed macromolecule conformation near the wall of such a pore. In this case the adsorption on the aggregate surface may be considered as adsorption on a rough or highly porous surface.

Recently, the adsorption of polymers on rough surfaces was investigated in terms of fractal geometry. This approach permits finding a simple relationship between adsorption amount and adsorbent or adsorbate particle size. Particularly, Pfeifer, Farin, and Avnir^{5,15} and then Farin and Avnir⁶ analyzed the adsorption using equations:

$$n_a \propto R^{D-3}, \quad (1)$$

$$n_a \propto N^{-D\nu} \quad (2)$$

where n_a is the number of adsorbed molecules per unit amount of adsorbent, R is the radius of adsorbent particles, N is degree of polymerization, D is fractal dimension of the surface, which show intrinsic surface irregularity ($D = 2$ characterizes a smooth flat surface; an excess $D > 2$ measures how fast similar surface wiggles repeat themselves upon progressive magnification of the surface), ν is the exponent in a power law between effective radius of polymer coil and N . They found that $D > 2$ and adsorbed chain conformation depended on the surface roughness. The authors mentioned that deviation from ideal $D = 2$ have been attributed to aggregation of adsorbent particles by adsorbed polymer molecules, resulting in interparticle porosity.⁵

In terms of the above-mentioned approach, the evaluation of adsorbed amount and determination of polymer adsorption isotherms become important characteristics of adsorption on the ultrafine particles. In this article we report how in some cases an adsorption isotherm may be used to characterize uniformity of polymer covering on the surface of ultrafine particles.

EXPERIMENTAL

Materials

PM–MA copolymer² ($M_n = 2800$, $M_w = 3200$) and labeled copolymer ($M_n = 3000$, $M_w = 4800$) with comonomer-dye 1-methacryloyl-amino-2-chlorine-4-(*p*-tolyl)-aminoanthraquinol were obtained from Organic Chemistry and Bio- and Dye Technology Departments of Lviv Polytechnic State University, respectively, and characterized as described in the previous article.¹ Copolymers of styrene and maleic anhydride (St-MA; 50 : 50 % mol) of different molecular mass (Fig. 4) were synthesized by solution radical polymerization with chain transfer agent and purified by multiple reprecipitation. St–MA copolymers were used as model polymers because PM–MA copolymers within wide limits of molecular mass are inaccessible to specific features² of PM copolymerization.

Powders of TiO₂ (industry pigment), ZnO (industry pigment), Al₂O₃ (reagent grade), CaCO₃ (reagent grade), aerosil (industry product), and quartz powders (QP), prepared by milling of quartz glass, were treated by 2-propanol and dried at 120°C at residual pressure of 10 mmHg.

Table I Specific Surfaces of Adsorbents

Adsorbent	Average Radius of Particles (μm)	Specific Surface (m^2/cm^3) Measured by		
		Adsorption N_2	Sedimentation Method	Adsorption of PM-MA
QP ₁	50	—	0.06	0.12
Al ₂ O ₃	7.4	—	0.3	0.8
QP ₂	5.5	—	0.42	1.0
CaCO ₃	0.50	6.0	1.1	3.2
ZnO	0.16	18.8	2.7	6.0
TiO ₂	0.13	23	4.3	6.4
aerosil	0.01	300	—	1.8

The specific surfaces of the powders as measured by sedimentation method and by N_2 adsorption are given in Table I. The average diameter ($2R$) for particles of aerosil, TiO_2 , ZnO, and CaCO_3 was calculated from the specific surface magnitude obtained by N_2 adsorption and for particles of QP and Al_2O_3 R was computed from the value of the specific surface, estimated by sedimentation analysis.

Solvents 2-propanol and 1,4-dioxane of reagent grade were used as received.

Adsorption Experiments

The adsorption of the copolymer was performed by adding 10 mL of polymer solution to 2.5 g of a powder (0.25 g in case of aerosil), followed by agitation for 2 h. Then the suspension was centrifuged and the concentration of the copolymer in the solution was determined by UV-visible spectra measurements for the labeled copolymer near the 450 nm band. The surface excess of the polymer Γ was calculated as

$$\Gamma = \frac{G^0(c^0 - c)}{m} \quad (3)$$

where G^0 is the weight of the solvent before the adsorption, c^0 and c is the weight of the polymer per unit weight of the solvent before and after the adsorption respectively, m is the weight of the adsorbent.

After centrifuging, the powder was separated, dried, and the value of the copolymer on the surface per unit weight (a^w) or volume (a^v) of the powder was evaluated by pyrolysis at 500°C . With the exception of the adsorption on aerosil the statistical error estimation showed very close values for these two methods of analysis. The relative

error was not more than 10%. The difference between Γ and a^w was very high for the adsorption on aerosil (see below).

RESULTS AND DISCUSSION

Effect of the Particle Size

As shown in Figure 2, for particles with the radius lower than $2.5 \mu\text{m}$ the amount of adsorbed polymer per unit surface of powders a^s (calculated on the basis of specific surface measured by means of sedimentation method for QP₁, QP₂, and Al_2O_3 and by N_2 adsorption for all other powders) (see Table I) decreases with decreasing of particle size of adsorbents. Adsorbents of different nature fit this relationship. In the previous article we found out that the adsorbent nature has no substantial

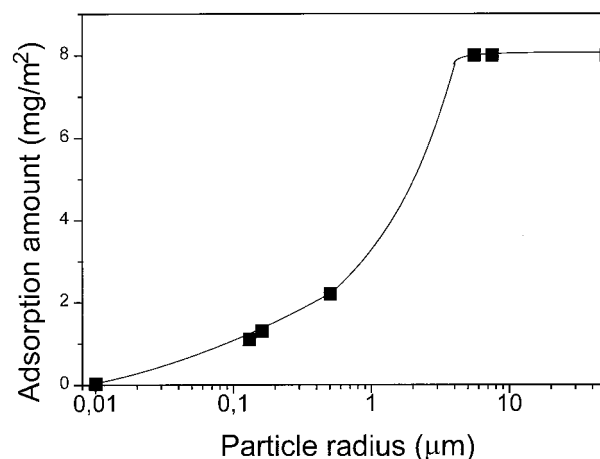


Figure 2 Plato adsorption amount (a^s) of PM-MA (25°C , 2-propanol) as a function of particle radius of different adsorbents (magnitudes of radius corresponds to the data of Table I for presented adsorbents).

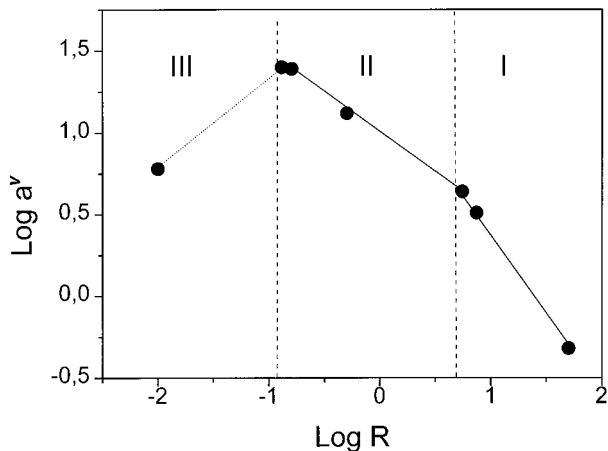


Figure 3 Plato adsorption amount (a^v) of PM-MA (25°C, 2-propanol) per unit volume of an adsorbent as a function of particle radius of different adsorbents (magnitudes of radius corresponds to the data of Table I and Figure 2 for presented adsorbents).

effect on PM-MA adsorption. From the replotted data as a^v (per unit volume of adsorbent, because we used adsorbents of different density) vs. particle radius on logarithmic scale (Fig. 3), one can see three regions on the curve: I—high values of $R > 2.5 \mu\text{m}$ and fractal dimension $D = 1.9$ calculated with eq. (1); II—intermediate region with $D = 2.5$ for $0.1 \mu\text{m} < R < 2.5 \mu\text{m}$, and III—the region where eq. (1) is not valid for ultrafine particles with R about 10 nm. Obviously, the surface is planar for the adsorption on large-sized particles (region I). We presumed that fractal behavior of medium-sized powders (region II) is caused by aggregation. The aggregates have pores (interparticle space) that are smaller than the characteristic length of the macromolecular chain. In the region III it is expected that the aggregation of ultrafine particles is governed by other mechanism as in the region II.

Effect of the Molecular Mass of the Polymer

A Γ vs. N plot is shown in Figure 4 for the adsorption of St-MA copolymers of various molecular mass on ZnO powder. There are two regions on the plot. The $\Gamma - N$ relationship is different for high molecular mass polymers and oligomers. In order to $n_a = \Gamma/M_n$, eq. (2) turns into

$$\Gamma \propto N^{1-D\nu} \quad (4)$$

Calculation of experimental data in Figure 4 with eq. (4) yields $D\nu = 0.57$ and 0.79 for both

regions of the plot respectively. If we used Flory's exponent value $\nu = 0.5$, we would not obtain reasonable magnitude D for both cases. From the data in Figure 3 we assumed that $D = 2.5$ (at least for low molecular mass polymers) and computed with eq. (4) values $\nu = 0.23$ and $\nu = 0.32$ for low and high molecular mass regions, respectively. Thus, the relationship between the cross-section of adsorbed macromolecules and the degree of polymerization differs for short and long chains.

It is known that macromolecules with high molecular mass are more active in adsorption. Nevertheless, we obtained the opposite result. We measured the intrinsic viscosity of St-MA solution (25°C, 1,4-dioxane) before $[\eta] = 0.1 \text{ dL/g}$ and after $[\eta] = 0.2 \text{ dL/g}$ adsorption. Thus, some fraction of large macromolecules was not able to permeate into interparticle space in aggregates. The particle aggregation was also suggested to employ for the explanation of such behavior.

Effect of the Agitation and Adsorbent Concentration

The presumption about the effect of aggregation was proved by investigation of PM-MA adsorption in the experiments with different kinds of agitation and various adsorbent (aerosil) concentrations. As shown in Figure 5, treatment of QP₂ suspension during adsorption with ultrasonic bath causes the increase of the adsorption amount. The effect of adsorbent particles concentration is excellently pronounced for aerosil (Fig. 6). The increase of aerosil concentration enhances

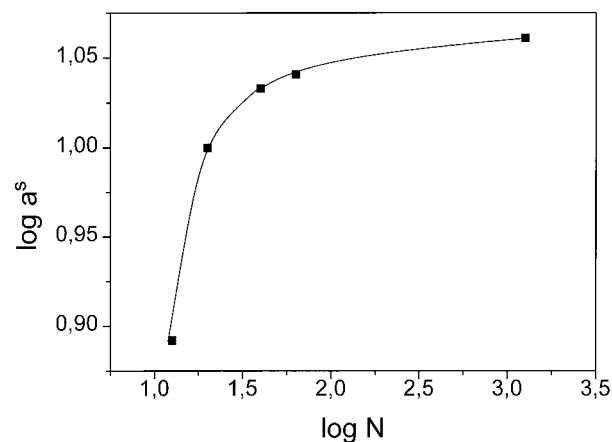


Figure 4 Plato adsorption amount (Γ) of St-MA on ZnO (25°C, 1,4-dioxane) as a function of degree of polymerization.

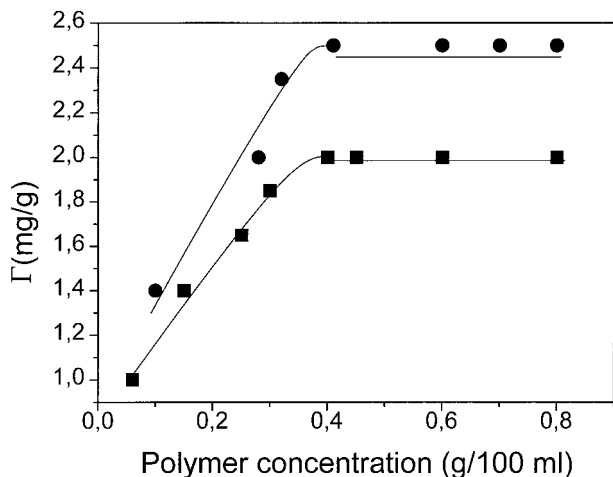


Figure 5 Effect of agitation on PM-MA adsorption on QP₂: (■) ordinary mixer; (●) ultrasonic bath.

aggregation and decreases adsorption. Ultrasonic treatment increases adsorption.

Adsorption Isotherms

For the adsorption in a binary system the equation of mass balance is given¹⁶:

$$\frac{n^0 \Delta x_1}{m} = n_1^s (1 - x_1) - n_2^s x_1 \quad (5)$$

where, $n^0 = n_1^0 + n_2^0$, $\Delta x_1 = x_1^0 - x_1$, n_1^0 and n_2^0 amount of moles of the component 1 and 2, respectively, in the solution before the adsorption, and mol fraction of the component 1 in the solution before and after the adsorption, respectively, and amount of adsorbed moles of the component 1 and 2, respectively, per unit weight of adsorbent after the adsorption.

For polymer adsorption it is more convenient to use weight concentration of the components: $c^0 = a^0/G^0$, $c = a/G$, where a^0 and G^0 are the weight of the polymer and solvent, respectively, before adsorption, a and G are the weight of the polymer and solvent, respectively, after adsorption. Then $n_1^0 = a^0/M_1$, $n_1^s = a^w/M_1$, $n_2^0 = G^0/M_2$, $n_2^s = G^w/M_2$, where a^w and G^w are the weight of adsorbed polymer and solvent, respectively, per unit weight of the adsorbent, M_1 and M_2 are molecular mass of the polymer and solvent, respectively. We may presume that for polymer adsorption $a^0 < G^0$, $a < G$, $M_2/M_1 < 1$. Taking into account what is mentioned above, from eqs. (5) and (3) we can obtain the following equation:

$$\Gamma \approx a^w - cG^w \quad (6)$$

In the case of polymer adsorption, c is within limits from 0.001 to 0.1 g/g and $a^w > G^w$. Consequently,

$$\Gamma \approx a^w \quad (7)$$

and the adsorption isotherm is a Langmuir-type isotherm (Fig. 5). At high concentration of polymer eq. (6) was proposed by Reháček¹⁷ and then by Konno with co-workers¹⁸ to investigate the composition of adsorbed layer using isotherm with extremum. Such shape of the isotherm is caused by different signs of terms in eq. (6).

We also obtained the isotherm for adsorption of PM-MA copolymer on aerosil but at relatively low concentration of the polymer (Fig. 7). The extremum should not be caused by the effect of the second term of eq. (6) at such low polymer concentration. Moreover, the curve on the plot goes down to negative Γ values while a^w values are positive. We presumed that aggregation brings about the extremum due to pores that are inaccessible for the polymer and accessible for the solvent. In this case eq. (6) transforms into

$$\Gamma \approx a^w - c(G^w + \rho V_a) \quad (8)$$

where V_a is the volume of pores per unit weight of the adsorbent inaccessible for the polymer, ρ is the density of the solvent.

Considering that $\rho V_a > G^w$, we employed eq. (9),

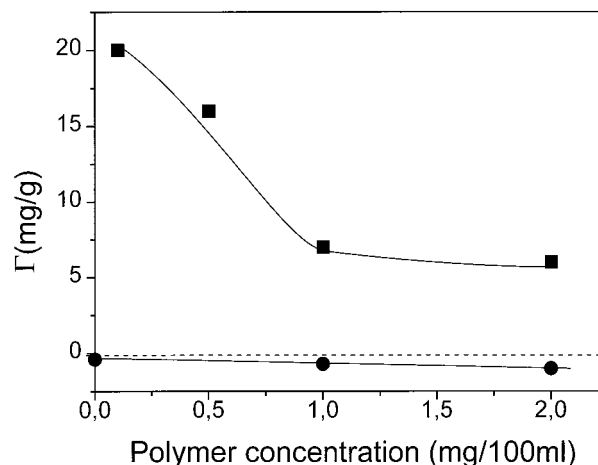


Figure 6 Effect of aerosil concentration and agitation on PM-MA adsorption (25°C, 2-propanol): (●) ordinary mixer; (■) ultrasonic bath.

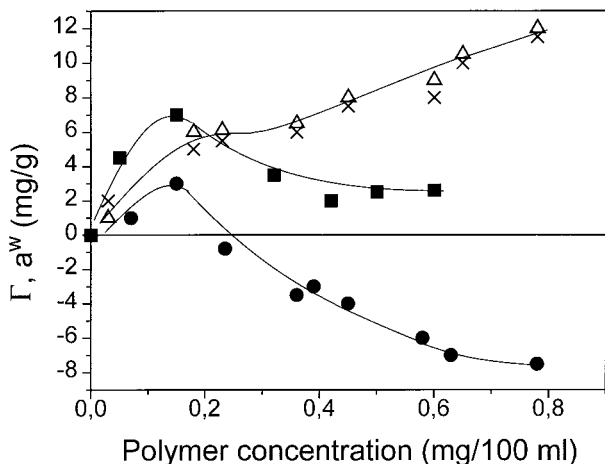


Figure 7 Experimental and transformed with eq. (9) individual (a^s) and surface excess (Γ) isotherms of PM-MA adsorption on aerosil (25°C, 1,4-dioxane): (●) Γ isotherm with ordinary agitation; (■) Γ isotherm with ultrasonic treatment; (Δ) a^w isotherm with ordinary agitation; (\times) a^w isotherm with ordinary agitation transformed from Γ isotherm with eq. (9).

$$G \approx a^w - c\rho V_a \quad (9)$$

to calculate values of a^w (see in Fig. 7 the curve with symbols shaped as \times) and $V_a = 2.4 \text{ cm}^3/\text{g}$ for the experiment at ordinary agitation. V_a was computed as a slope of the plot Γ vs, c of going down part of the curve after the maximum. As shown in this plot, a^s directly evaluated from the experiment is in good agreement with the calculated curve. It is clear that obtained V_a value is the some average characteristics of the structure of the suspension, because this parameter could be different at each point of the isotherm and very sensitive to the condition of the preparation of the suspension. We should also notice that the suspension structure, and consequently V_a , depends on the size distribution function of the aggregated particles.

The isotherm obtained at ultrasonic treatment is also presented in the Figure 7. In the last case the ultrasonic treatment affect the access of the "walls of pores" for the polymer and increasing adsorption.

Effective Surface of Adsorbent

The above-mentioned results show that the specific surface of ultrafine particles should be considered in terms of fractal geometry. Otherwise, we may introduce a notion of effective (apparent) ad-

sorbent surface that corresponds to a definite kind of adsorbate macromolecules. For instance, it was found out that plateau value of PM-MA adsorption (a^s) on the surface of silicon wafers evaluated by means of null ellipsometry method¹⁹ was about $4 \text{ mg}/\text{m}^2$. Consequently, we may use for a^s a value of $4 \text{ mg}/\text{m}^2$ as a primary standard (taking into account a poor effect of surface nature on PM-MA adsorption¹) to estimate the effective surface of other adsorbents. The evaluation based on this approach is presented in Table I. It turned out that the effective surface of aerosil is 150 times lower than the specific surface estimated by the N_2 adsorption method. Obviously, PM-MA adsorbs on the surface of aggregates of the size about $0.5\text{--}1 \text{ }\mu\text{m}$.

CONCLUSIONS

The adsorption amount of the investigated polymer decreases with decreasing of particle size of adsorbent. Effective agitation increases the adsorption. We explained these effects by aggregation of ultrafine adsorbent particles. Interparticle space (pore) in the area of contact of neighboring particles is inaccessible for the polymer and accessible for the solvent. For quantitative description of this phenomena we employed terms of fractal geometry and notion of effective surface of adsorbent. Nevertheless, the obtained results showed that the evaluation of the polymer adsorption value per unit surface of an adsorbent is essentially complicated because of the uncertainty of the values of effective specific surface. Even small change of the adsorption conditions (e.g., ultrasonic treatment of the suspension) change the kinetics of the structure formation in the suspension and, consequently, polymer adsorption amount. The effective specific surface decreases also with increasing molecular mass of the polymer. The effect of molecular mass is different for small ($N < 100$) and large ($N > 100$) macromolecules.

From a practical point of view the results obtained are important for the consideration of advantages and disadvantages of various methods of particle covering with polymers. It is clear that synthesis of covering *in situ* is more preferable to get uniform covering of each particle because of substantially higher accessibility of interparticle space in the aggregate for molecules of a monomer than macromolecules.

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