

Sorption Characteristics of Porous Styrene-Divinylbenzene Copolymers Filled with Modified Silica

Yulia Bolbukh,^{*1} Pavlo Kuzema,¹ Valentin Tertykh,¹ Barbara Gawdzik²

Summary: The structural parameters of porous styrene-divinylbenzene copolymer, unfilled and filled with silica containing surface trimethylsilyl and silicon hydride groups were studied by aniline and *p*-chloroaniline adsorption. It has been shown that embedding of chemically modified silica affects the material porosity and decreases the copolymer swelling in benzene.

Keywords: adsorption; aniline; copolymer; silicas; styrene-divinylbenzene

Introduction

Polymeric microspheres based on copolymer styrene cross-linked with divinylbenzene are attractive materials for a wide number of applications including stationary phases for separation, biomedical devices, coating additives or controlled release systems. The main disadvantage of the polystyrene phases is their sensitivity to solvent changes (shrinkage or swelling) associated with the presence of pores. Embedding of inorganic nanoparticles into these polymers presumably will allow improving their operational characteristics. The most commonly used filler for such systems is high-disperse silica. It is possible to partially hydrophobize the filler surface, for instance with trimethylsilyl (TMS) groups, in order to increase its compatibility with polymer while keeping its structure ability^[1]. In the presence of surface silicon hydride (SiH) groups the cross-linked structure is achieved due to formation of hydrolytically stable polymer – silica bonds during hydrosilylation of unsaturated

monomer groups^[2]. Thus, the presence of TMS and SiH groups on silica surface presumably will allow one to obtain high filler dispersion and chemical structuring of a composite.

The aim of this work was to investigate the change in the internal morphologies of styrene-divinylbenzene copolymers related to the presence of silica fillers with different amount of chemically active surface groups. Adsorption method was used to estimate the solvent resistance since, on our opinion, it is the most suitable approach to study such systems.

Experimental Part

Styrene (St), Divinylbenzene (DVB) (Merck), fumed silica with a specific surface area of 200 m²/g (Kalush, Ukraine), trimethylchlorosilane and triethoxysilane (“Kremnepolimer”, Ukraine), aniline and *p*-chloroaniline (“Ukrorgsintez”, Ukraine) were applied.

Porous St-DVB (molar ratio 0.8:0.2) spheres were obtained via suspension-emulsion polymerization^[3] without and in the filler presence. As filler a fumed silica with attached TMS or both TMS and SiH groups was used. The filling degree was 13 wt%.

The copolymer internal structure resistance to solvent action was studied by treatment with benzene at 20 °C during two

¹ O.O. Chuiko Institute of Surface Chemistry, National Academy of Sciences of the Ukraine, General Naumov Str. 17, 03164 Kyiv, Ukraine
Fax: (+38) 044 4243567;
E-mail: bolbukh@yahoo.com

² Faculty of Chemistry, Maria Curie-Skłodowska University, M.C. Skłodowska Sq. 3, 20031 Lublin, Poland

days and following adsorption analysis. The swelling degree was determined as difference in adsorption capacity before and after the treatment with solvent. Adsorption of aniline or *p*-chloroaniline was performed at 20 °C from aqueous solution in a concentration interval 0.055–0.0027 or 0.3×10^{-3} – 0.006×10^{-3} mol/l, respectively. Concentration of the adsorbate in solution was determined by photometric analysis using Specord M-40.

Adsorption isotherms were treated using the model from the theory of the volume filling of micropores (TVFM). Pore volume was calculated using the following formula^[4]: $V_p = A_{\max} V^*$, where A_{\max} – limiting adsorption; V^* – molar volume of an adsorbate. A_{\max} was determined from linearized adsorption isotherm in coordinates $\ln A = f(\ln(C_s/C_{eq}))^n$, where A – adsorption, mmol/g; C_s – adsorbate solubility limit, mol/l; C_{eq} – equilibrium concentration, mol/l;

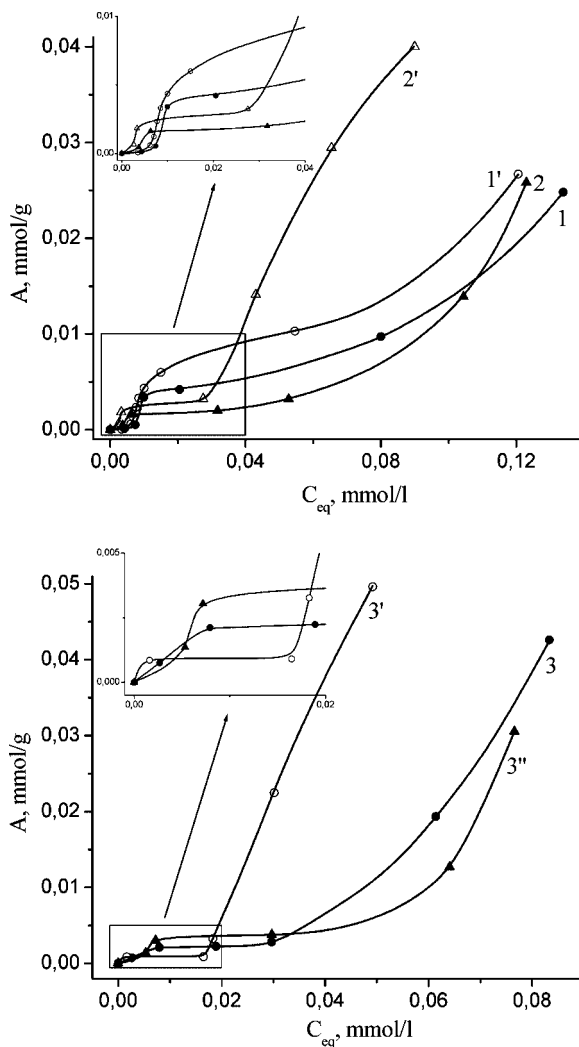


Figure 1.

The isotherms of *p*-chloroaniline adsorption on porous St-DVB spheres: 1 and 1' – initial and swelled unfilled copolymer; 2 and 2' – initial and swelled copolymer filled with 30% trimethylsilylated silica; 3, 3', 3'' – respectively initial, swelled and relaxed copolymer filled with 30% trimethyl- and 30% hydridesilylated silica.

$n = 1$ –6 depending on the adsorbent structure. Parameter n for each composite was evaluated from the characteristic change of correlation coefficient for the appropriate linearized isotherm (R) and adequacy of pore volume values. Porosity (P) was calculated as ratio of pore volume and the total volume. The predominant factor of resistance to solvents of the copolymer internal structure was considered as relative change of pore volume at swelling (V_p (swelled)/ V_p (initial)).

Results and Discussion

The isotherms of *p*-chloroaniline and aniline adsorption are given in Figures 1 and 2, respectively. All the isotherms are attributed to L-type by Giles classification^[5] and therefore they may be characterized by Freundlich or Langmuir equation.

However, it has been shown^[6] that *p*-chloroaniline adsorption on porous St-DVB spheres is described satisfactorily by TVFM equation. The results of the

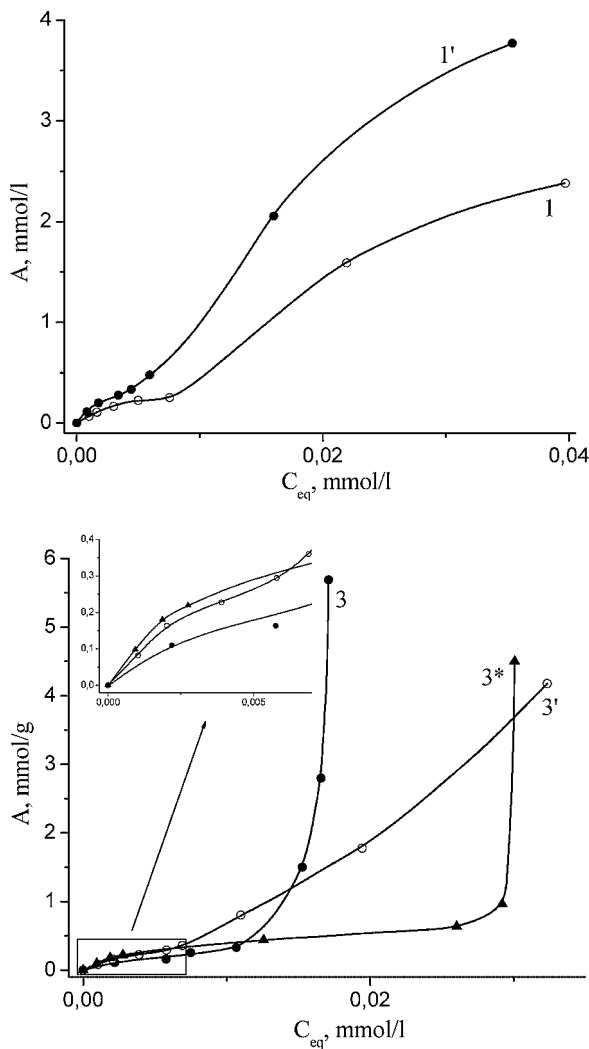


Figure 2.

The isotherms of aniline adsorption on porous St-DVB spheres: 1 and 1' – initial and swelled unfilled copolymer; 3, 3', 3* – respectively initial, swelled and re-swelled copolymer filled with 30% trimethyl- and 30% hydride-silylated silica.

Table 1.Structural parameters of St-DVB spheres derived from the treatment of *p*-chloroaniline adsorption isotherms.

N	Sample		V_p , cm ³ /g	n	R	P
1	DVB-St unfilled	initial	0.05	2	0.93	0.007
		swelled	0.64	2	0.89	
2	DVB-St/silica (30% TMS groups)	initial	0.18	1	0.82	0.020
		swelled	0.76	1	0.89	
3	DVB-St/silica (30% TMS, 30% SiH groups)	initial	0.01	3	0.86	0.002
		swelled	0.02	2	0.73	
		relaxed	0.03	2	0.96	

isotherms treatment using TVFM model are shown in Table 1 and 2 respectively for *p*-chloroaniline and aniline adsorption. All the St-DVB/silica composites under study demonstrate an increase in solvent resistance since the value of relative change of pore volume at swelling (V_p (swelled)/ V_p (initial)) is less for them in comparison with the unfilled sample.

Pore volume for the unfilled St-DVB is increased by more than order after swelling (Table 1, sample 1). For St-DVB filled with modified silica the calculations demonstrate (Table 1, samples 2, 3) that filling with trimethylsilylated by 30% silica leads to formation of more porous structure with relatively low benzene resistance whereas the presence of filler containing 30% of surface SiH groups along with above mentioned quantity of TMS groups decreases the porosity and increases swelling resistance.

After relaxation the porosity of sample 3 increases as a consequence of additional interstices formation.

The porosity value as well as the parameter n derived from the *p*-chloroaniline adsorption data differ from those in the case of aniline adsorption (Table 1, 2) indicating the higher affinity of the latter to the surface of St-DVB copolymer. However, the tendency of solvent resistance

increase at filling with modified silica is also observed (Table 2, sample 3). It is interesting to note a decrease of pore volume of re-swelled St-DVB composite even in comparison with the unswelled one (Table 2, Figure 2, samples 3* and 3). At this, the parameter n also decreases. It may be explained by a decrease of aniline affinity to the surface of re-swelled sample from the one hand, and by pores breakdown (structural rearrangement while drying and re-swelling) – from the other.

On basis of the data from literature^[7] and adsorption results obtained one may assume that surface of partially trimethylsilylated silica decreases the degree of St-DVB copolymerization. At this, formation of loosened polymer layer near the filler surface and flexible, easy deformable macromolecules in composite bulk is occurred. The presence of SiH groups, though decreases the porosity of St-DVB composite, but increases benzene resistance of copolymer structure as a result of more dense packing and chemical attachment of macromolecules onto filler surface.

Conclusion

The morphological changes of St-DVB copolymer spheres are reflected in the

Table 2.

Structural parameters of St-DVB spheres derived from the treatment of aniline adsorption isotherms.

N	Sample		V_p , cm ³ /g	n	R	P
1	DVB-St unfilled	initial	0.24	3	0.95	0.032
		swelled	0.48	3	0.97	
3	DVB-St/silica (30% TMS, 30% SiH groups)	initial	0.32	4	0.81	0.039
		swelled	0.39	3	0.92	
		re-swelled	0.28	2	0.78	

change of the isotherm shape and the adsorption capacity with respect to aniline and *p*-chloroaniline. The filling with modified silicas containing surface TMS or TMS and SiH groups results in an increase of St-DVB copolymer swelling resistance in benzene. However, the presence of SiH groups on silica surface leads to formation of loosened structure with unstable porous characteristics while reuse.

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