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Polyacrylamide-Grafted Silica as Special Type of Polymer-Colloid Complex

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Summary: Structure and properties of polyacrylamide-grafted silica have been investigated with the help of thermal analysis methods, NMR spectroscopy and by measuring the ability solubilization in benzene when compared with homopolymer polyacrylamide (PAA). More homogeneous structure, low rigidity and density of packing have been revealed for the polymer shell. PAA form a dense polymer shell, which interact with silica surface through H-bonds. ^{1}H NMR spectroscopy suggests no influence of silica particles on PAA stereoregularity. PAA-grafted silica considered as a special type of polymer-colloid complex where polymer chains are covalently bound to silica with one end and polymer segments along the chain are hydrogen bound to the particle surface.

Keywords: polyacrylamide-grafted silica; polymer shell; properties; structure

Introduction

Modification of inorganic surface through the use of physically adsorbed or grafted macromolecules constitutes an important means by which tailor both surface and polymer at interface properties governing, for instance, stabilization of colloidal dispersions adhesion, lubrication, biocompatibility.[1-4] A large body of knowledge is now available on polymers grafting onto nanoparticles.[5-8] Polymer-grafted particles synthesis usually includes the preliminary chemical modification of particle surface or polymer.[5,6,8] We have performed the radical graft polymerization of acrylamide (AA) onto silica nanoparticles using ceric ions. The unification of sorption ability of colloid particles surface and binding properties of long polymer chains in PAA-grafted silica produces its high flocculative capability during clarifying of model kaolin suspension (R=6,5 μm, C=30 kg m^{-3}) and at the coagulative-flocculative process of natural water clearing.[9,10] In the present work we consider some structure features and properties of PAA-grafted silica and peculiarities of PAA shell.

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Structure and properties of PAA-grafted silica

In a previous paper we have reported the grafting of PAA onto poly(vinyl alcohol) backbone, initiated with radicals formed by the redox reaction of ceric ion and alcoholic hydoxyl groups under nitrogen.[11] In the present paper to graft PAA onto silica the same cerium-ion-initiated solution polymerization technique have been used. AA polymerization in this process was initiated by redox system consisting of ceric ion and silanol group, which is naturally abundantly present on silica. Silica nanoparticles used was Aerosil A-175 with average hydrodynamic diameter of sol particles 22 nm. The molecular weight of grafts was estimated to be 1160000 from the intrinsic viscosity. The grafts number N was calculated to be on average 53 grafts per 1 silica particle from elementary analysis data, but considering the water content in polymer-grafted particle.[12] The confirmation of silica availability in grafted product was carried out by elemental analysis. Grafted product was investigated together with PAA sample ($\overline{M}_v$=1250000).

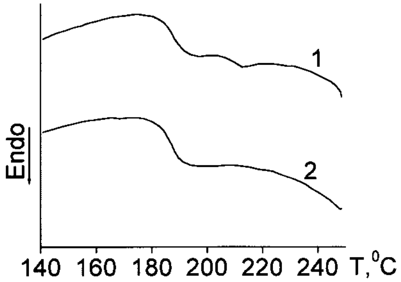

Figure 1. DSC thermograms for PAA (1) and PAA-grafted silica (2) (second run after heating to 160 °C and rapid cooling)

DSC thermograms obtained by differential scanning calorimetry (DSC) at the heating rate 16 °C/min with the help of Du Pont 1090 thermal analyzer are shown in Figure 1 and the data of thermal transitions are presented in Table 1. The glass transition temperature of PAA-grafted silica was determined to be lower than that for PAA but transition occurs in more narrow temperature interval (ΔT_g). This fact and the lack of *ll*-transition for PAA-grafted silica suggest more homogeneous structure, lesser rigidity and density of packing for PAA graft chains than for homopolymer.

Table 1. Thermal transition temperatures.

Name	Tg °C	ΔT_g °C	T_{ll} [1] °C	ΔT_{ll} °C	ΔC_p [2] J·g^{-1}·K^{-1}
PAA	188	13	206	14	0,65
PAA-grafted silica	186	11	-	-	0,67

[1] *ll*-transition temperature

[2] Heat capacity jump of α-relaxation transition

Thermal behavior of PAA-grafted silica was investigated by dynamic thermogravimetric analysis (DTA) in the non-isothermal regime on Q-1500 "quasi" technique of F.Paulik, G.Paulik, L.Erdey system at heating rate 2,5 °C/min. Weights of ~ 20 mg were used. Parameters of thermooxidative decomposition obtained from experimental TG, DTG and DTA curves are gathered in Table2. The common analogy between PAA-grafted silica and PAA decomposition in air that occurs in three stages is observed. But such differences for polymer-grafted particle exist: T_d (T_{in} of stage I) falls; ΔT of stage I, which accompanied by endothermic effect increases; ΔT of stage II, which accompanied by exothermic effect decreases; ΔT of stage III, which is accompanied by maximum exothermic effect extends; common temperature interval of decomposition falls. The thermostability reduction of filled polymers is well known.

Table 2. Parameters of thermooxidative decomposition.

Name	Stage	$T_{\mathrm{in}} \div T_{\mathrm{f}}$ 1) °C	ΔT 2) °C	T_{max} 3) °C	W 4) %	Thermal effect °C	Residual %
PAA	I	256-344	88	302	16.5	endo	
	II	344-449	105	404	21.2	exo, 404	
	III	449-618	169	558	52.4	exo, 558	9.9
PAA-grafted silica	I	236-331	95	289	18.2	endo	
	II	331-406	75	376	18.1	exo, 374	
	III	406-587	181	535	60.3	endo	3.4

1) Initial and final temperatures.
2) Temperature interval.
3) Temperature of the maximum decomposition rate.
4) Weight loss.

Table 3. Formal kinetic parameters of two stages of thermooxidative decomposition.

Name	Stage	$T_{\mathrm{in}} \div T_{\mathrm{f}}$ 1) °C	E 2) kJ/mol	n 3)	Z 4) 1/s	k 5) 1/s
PAA	I	256-344	143,9	1,15	$1{,}34 \cdot 10^{12}$	0,113
	II	344-449	165,2	1,40	$6{,}13 \cdot 10^{11}$	0,110
PAA-grafted silica	I	236-331	218,5	2,41	$5{,}96 \cdot 10^{19}$	0,292
	II	331-406	178,86	8,6	$6{,}32 \cdot 10^{61}$	42,77

1) Initial and final temperatures.
2) The activation energy.
3) The order of reaction.
4) The frequency factor in the Arrhenius equation.
5) The rate constant of decomposition.

Formal kinetic parameters *E, n, Z* and *k* of two first decomposition stages determined by computer processing of experimental data from TG and DTG curves using Arrhenius equation in the matrix form and the least-squares method are presented in Table 3.[13]

Using literature and own experimental data we have explained the chemical transformations occurring during PAA decomposition in air previously.[14-16] The maximum values of formal kinetic parameters for PAA-grafted silica on the stage I of decomposition when comparing with PAA (Table 3) suggest interaction of grafts with silica through H-bonds, producing formation of separate cross-links between PAA graft chains and silanol groups at the temperature influence before the beginning of destruction. The largest values of formal kinetic parameters for PAA-grafted silica on the stage II of decomposition (Table 3) when the process of polymer oxidation occurs, suggest more weak interaction between PAA graft chains comparing with homopolymer producing high rate of the solubility and diffusion of oxygen in the polymer bulk.

Investigation of benzene solubilization by aqueous polymer-grafted particle solutions was carried out by refractometry method.[17] The determination of values (Figure 2) and parameters (Table 4) of benzene solubilization was described previously.[17] Solubilization curve for PAA (Figure 2, curve 1) has two steps due to coiling of PAA macromolecules in the solubilization process at benzene concentration C=22 kg/m^3. Benzene binding with SiO_2 particles arises from formation of H-bonds between benzene π-electron system and

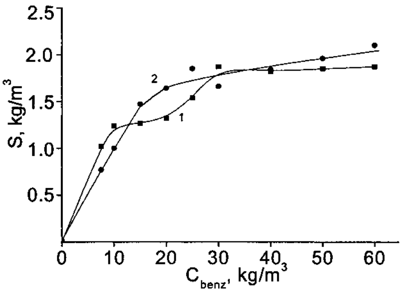

Figure 2. Value of solubilizaton *versus* benzene concentration with PAA (1) and PAA-grafted silica (2) aqueous solutions.

Table 4. Parameters of benzene solubilization with aqueous homopolymer and polymer-grafted particle solutions.

Name	S_{lim}	S_{red}	N 1)	V 2)
	kg/m^3	kg/m^3	mol_{benz}/mol_{sample}	nm^3
PAA	1.83	0.08	1505	135
SiO_2 3)	1.89	0.14	4450 4)	-
PAA-grafted silica	1.70	-	-	-

1)Number of benzene molecules bound by one sample macromolecule.
2)Size of hydrophobic regions.
3)Literature data. [18]
4)Number of benzene molecules bound with one SiO_2 particle.

silanol groups of silica surface. The absence of surplus benzene solubility in PAA-grafted silica aqueous solution arises from destruction of hydrophobic regions in polymer shell due to PAA interaction with particles surface and formation of dense polymer shell, which prevents benzene transport to SiO_2 surface.

^1H NMR spectra were recorded with a Varian Mercury-400 spectrometer operating at 400 MHz. The elucidation of PAA homopolymer stereoregularity (^{13}C NMR spectroscopy) has been performed previously using literature data where authors obtained good resolved ^{13}C NMR spectrum for low-molecular-weight PAA.[19,20] The resulting spectrum showed the methylene, methine and carbonyl carbons of head-to-tail vinyl polymer. Polyacrylamide obeys Bernoulli statistics with $P_m = 0.43$, which is not unlike other vinyl polymers. As we have not obtained the good resolved ^{13}C NMR spectrum for homopolymer, PAA-grafted silica was investigated by ^1H NMR spectroscopy (Figure 3).[20] From the overall line shapes and peak percentage contribution to intensity of methine and methylene ^1H signals in the limits of integrating errors it is evident that the results obtained for PAA hold for PAA-*grafted.* Insignificant differences in peak positions are observed due to their measurements referencing to H_2O. So the microstructures of polymer formed at homopolymerization and at grafting polymerization onto silica are not differed. The possible explanation for this is few contacts of growing PAA chains with SiO_2 when only sufficiently long growing chain part contact with silica. It is possible when the interaction is week or when the steric hindrances exist. But it is well known about great affinity of PAA to silica surface. So due to the steric hindrances there are few contacts of growing PAA chain with SiO_2 and sufficiently long unbound parts of grafted macromolecule.

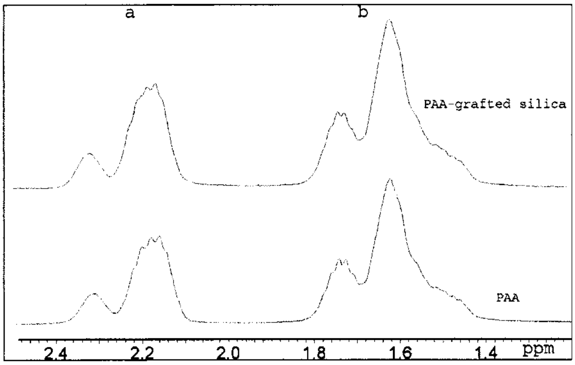

Figure 3. Methine (a) and methylene (b) ^1H resonances of PAA (0.01 g/cm^3 solution in D_2O) and PAA-*grafted* in PAA-grafted silica (0.001 g/cm^3 solution in D_2O).

Conclusion

The main conclusions from our studies are: (i) more homogeneous structure, lesser rigidity and density of packing are observed for PAA-grafted than for PAA; (ii) the cooperative system of H-bonds exist between silica surface and PAA which form the dense polymer shell; (iii) the stereoregularity of PAA-grafted and homopolymer are not differed. Graft polymerization of PAA onto silica particles results in polymer-colloid complex formation of special type where polymer chains are covalently bound to silica with one end, where are a few contacts of grafted chains with particle surface through H-bonding and sufficiently long unbound parts of grafted chains (loops and tails) which interacts between themselves (Figure 4).

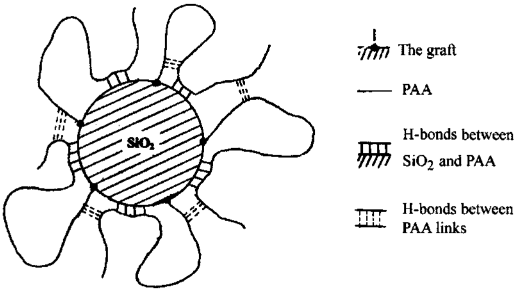

Figure 4. Schematic model for PAA-grafted silica.

[1] N.Tsubokawa, T.Umeno, *J. Jap. Soc. Colour. Mater.* **1991**, *64*, 751.
[2] A.Dorinson, K.C.Ludema, "*Mechanisms and Chemistry in Lubrication*", Elsevier, Amsterdam 1985.
[3] T.Okano, T.Aoyagi, K.Kataoka, K.Abe, Y.Sakurai, M.Shimada, *J. Biomed. Mater. Res.*1986, *20*, 919.
[4] M.I.Baraton, F.Chancel, L.Merhari, *Nanostruct. Mater.* **1997**, *9*, 319.
[5] M.L.Rong, Q.L.Ji, M.Q.Zhang, K.Friedrich, *Europ. Polym. J.* **2002**, *38*, 1573.
[6] Y.Shirai, N.Tsubokawa, *Reactive and Functional Polym.* 1997, *32*, 53.
[7] J.Liu, R.Pelton, A.N.Hrymak, *J.Coll. Int. Sci.* 2000, *227*, 408.
[8] Y.Shirai, K.Kawatsura, N.Tsubokawa, *Progr. In Organic Coat.* **1999**, *36*, 217.
[9] V.V.Goncharuk, I.M.Solomentseva, V.F.Skubchenko, T.B.Zheltonozhskaya, O.V.Demchenko, N.V.Kutsevol, V.G.Syromyatnikov, V,S.Bilyk, V,M.Olenchenko, UA 44968A **2002**.
[10] V.V.Goncharuk, I.M.Solomentseva, V.F.Skubchenko, T.B.Zheltonozhskaya, O.V.Demchenko, N.V.Kutsevol, V.G.Syromyatnikov, UA 36528 **2003**.
[11] B.V.Eremenko, M.L.Malysheva, O.D.Rusina, N.V.Kutsevol, T.B.Zheltonozhskaya, *Colloids Surfaces A: Physicochem Eng. Aspects.* **1995**, *98*, 19.
[12] C. L.McCormik, L. S. J.Park, *Appl. Polym. Sci.* **1985,** *30*, 45.
[13] O.V.Suberlyak, G. Yu.Uigeliy, *Dopovidy NAN Ukr.* **1998**, *11*, 150.
[14] W. M.Leung, D. E. J.Axelson, *Polym. Science.* **1987**, *25*, 1825.
[15] N. V.Kutsevol, T. B.Zheltonozhskaya, O. V.Demchenko, L. R.Kunitskaya, V. G.Syromyatnikov, *Vysokomol. Soed.* **2004,** *A46(5)*, 839.
[16] O.Demchenko, T.Zheltonozhskaya, J.-M.Guenet, S.Filipchenko, V.Syromyatnikov, *Macromol. Symp.* **2003**, 203,183.
[17] N.Zagdanskaya, L.Momot, T.Zheltonozhskaya, J.-M.Guenet, V.Syromyatnikov, *Macromol. Symp.* **2003**, 203,193.
[18] T.B.Zheltonozhskaya, O.O.Romankevich, N.V.Kutsevol, V.G.Syromyatnikov, *Proceed. of the 2th International Conf. On Carpathian Euroregion Ecology,* **1997,** Miskolc (Hungary), 149.
[19] J. E.Lancaster, , M. N. J.O'Conner,*Polym. Science: Polymer Letters Edition.* **1982**, *20*, 550.
[20] O.Demchenko, T.Zheltonozhskaya, A.Turov, M.Tsapko, V.Syromyatnikov, *Mol. Cryst. and Liq. Cryst., submited for publication.*