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Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 2. Grafting process onto silica

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Emulsion polymerization of ethyl acrylate has been carried out in the presence of two kinds of silica, either functionalized by treatment with methacryloylpropyltrimethoxysilane, or not. Both polymerization and grafting kinetics were followed. A part of the polymer is covalently grafted onto silica only if the latter is functionalized and the grafting process takes place at the beginning of the process. The grafted polymer is tightly linked to the silica surface as a succession of small-sized loops. High-molecular-weight non-grafted polymer is also produced with compressed conformation, its radius of gyration being much larger than the thickness of the polymer layer encapsulating the silica.

(**Keywords: encapsulated silica; poly(ethyl acrylate) latex; grafting process**)

INTRODUCTION

Grafting polymers onto the surface of inorganic particles is a field of growing interest. A lot of work has been done with the purpose of developing specific stationary phases for gas or liquid chromatography[1–3]. More recently, new applications have been studied such as supported catalysis[4,5], water treatment[6], encapsulation of inorganic particles in order to get them better dispersed in polymeric matrices[7], grafting bioactive compounds onto magnetic particles with spacer arms[8], etc.

Most of the work was carried out in solution, via two routes, which are grafting *from*, i.e. polymerization of monomer from active compounds (initiators, comonomers,...) covalently attached to the inorganic surface[9], or grafting *onto*, i.e. producing a polymer independently of the inorganic particles, with an end-group able to react with the functional groups of that surface, for instance silanol groups[10]. Various chemistry has been used in that connection, including radical[2–9], anionic[10] and cationic[11] polymerization.

This paper is devoted to the study of grafting from silica particles using a radical process, but in emulsion rather than in solution. Emulsion polymerization has been used more and more in recent years to encapsulate inorganic particles[12–15]. However, in most cases there is no actual grafting and the encapsulating polymer is believed to stay around the particles due to electrostatic interactions[16,17]. Recently, Caris *et al.* have reported a study where TiO_2 particles are first covered with titanates containing polymerizable groups and then engaged in emulsion polymerization so that covalent grafting can take place[18]. The work was recently extended to $CaCO_3$ also modified with titanate by Van Herk *et al.* [19] who have shown that about 20% of the polystyrene produced was tightly bound to the surface of $CaCO_3$. The route we have followed is quite different: It involves first the surface functionalization of silica, chosen as a model for inorganic particles, with a coupling agent carrying a polymerizable group, i.e. methacryloylpropyltrimethoxysilane (MPTMS) (*Scheme 1*). Then the modified silica is engaged in the emulsion polymerization of ethyl acrylate. The hybrid latex so prepared is finally used to obtain a film reinforced by the encapsulated silica particles. The mechanical properties of such films are compared with those of similar films also using encapsulated silica particles which have not been previously functionalized.

A few preliminary studies have been published. The first one[20] concluded that a non-ionic emulsifier was needed to avoid the formation of a pure polymer latex in addition to the silica. The use of hydrophobic monomers such as styrene or butyl acrylate did not lead to successful encapsulation. On the other hand, monomers with some hydrophilicity, such as methyl methacrylate or ethyl acrylate, behave more satisfactorily. Such results are in line with the fact that most of the previous studies have been carried out with monomers that are sufficiently soluble in water. The Japanese authors have worked chiefly with methyl methacrylate[12–14], while Hergeth *et al.*[15] used vinyl acetate. A second study[21] dealt with a kinetic study of ethyl acrylate polymerization in the presence of colloidal silica particles, with or without surface functionalization using a suitable non-ionic emulsifier, strongly adsorbed onto the silica surface, and suitable treatment of the functionalized silica, which allows a reasonably good dispersion of that silica in water. The quality of the encapsulation was estimated by comparison of the initial number of silica

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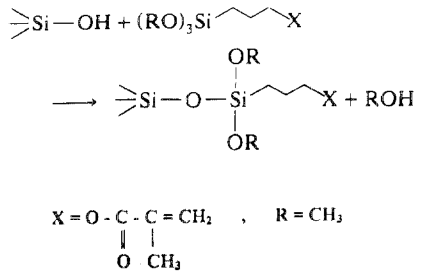


Scheme 1 Grafting process of MPTMS onto silica

particles with the final number of latex particles, both numbers being deduced from particle-size measurements. The ratio between these two numbers was around 1: it increased from 0.6 to 4 in the case of non-functionalized silica, and from 0.9 to 9 in the case of surface-modified silica, while the weight ratio monomer/silica was varied in both cases from 2 to 64. When that ratio is larger than 1, it means that some latex particles do not contain silica particles; while if the ratio is smaller than 1, there is a trend to encapsulate more than one silica particle in the latex particle. Although the contrast between the silica and the polymer in transmission electron microscopy was not good enough to check the encapsulation directly, these latexes are able to give fully transparent films, indicating an excellent dispersion of the silica particles. On the other hand, the mechanical properties of the two series of films were shown to be very different[22]. In order to understand these differences, it is necessary to answer the question of how the polymer may be linked to the silica particle. It is expected to be simply adsorbed in the case of non-functionalized silica and to be at least partly covalently bound when the silica has been functionalized with MPTMS. This paper is thus concerned with the characterization of the polymer, either adsorbed or grafted, and with a brief kinetic study of the grafting process. The first paper of the series describes in more detail the functionalization process and then the dispersion of the functionalized silica in water. The analysis and discusion of the mechanical properties is the subject of the following third paper.

EXPERIMENTAL

Materials

The non-functionalized silica is Ludox AS 40 from DuPont (diameter 22 nm). The functionalized silica has been prepared from commercial Aerosol A200V from Degussa (diameter 13 nm) as follows. An excess of MPTMS already partly hydrolysed ($8\,\mu$mol m^{-2}) is added to a suspension of silica in toluene (weight ratio 1/30), and the suspension is refluxed for 16 h under a N_2 atmosphere. After filtration and vacuum drying at moderate temperature (40°C or less), the powder is dispersed in a water solution of ammonia at pH 9.5 to which a small amount (0.4%) of isobutanol has been added as a dispersion agent. After sonication, a reasonably monodisperse population of particles of 37 nm diameter is obtained

All other materials are commercial products used without further purification except for distillation of the ethyl acrylate monomer (Kodak).

Emulsion polymerization

The 1.5 litre jacketed glass reactor was charged with the aqueous dispersion of silica. Then the non-ionic surfactant ($0.34\,\mathrm{g\,l^{-1}}$) was introduced in an amount lower than the one corresponding to saturation of the surface so as to avoid the formation of emulsifier micelles. Then degassing was carried out overnight under gentle stirring. The temperature was increased up to 60°C and then the initiator (potassium persulfate, $0.7\,\mathrm{g\,l^{-1}}$) was introduced. The stirring rate was fixed at 250 rpm and a continuous process of introduction of monomers at a rate of $0.34\,\mathrm{ml\,min^{-1}}$ for 2.5 h was started. The polymerization was carried out for 22 h, with sampling at various times up to 12 h to measure monomer conversion from the solid contents, particle size and grafted polymer characterization.

Characterization

Particle size was obtained from transmission electron microscopy. According to *Scheme 2*, the latex was first centrifuged to separate the serum, and then dried under vacuum. Toluene extraction for 8 h under reflux allows dissolution of the polymer that is simply adsorbed; the residual solid is the silica covered with grafted polymer. The latter can be separated only after destruction of silica with concentrated aqueous HF solution (40 wt%) at 50°C.

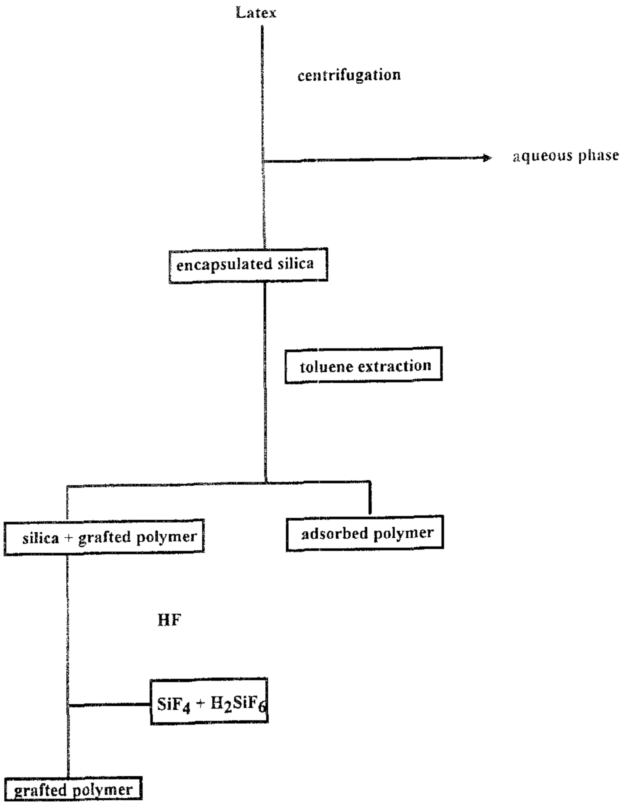
The molecular weight of the polymers (both adsorbed and grafted) and their radius of gyration were obtained by light scattering (Zimm plot).

RESULTS AND DISCUSSION

In order to get complete encapsulation of silica without formation of pure latex, a set of experimental conditions must be fulfilled. The amount of silica is chosen to have a number of particles similar to that generally used in emulsion polymerization (10^{16} to 10^{18} per litre). The concentration of surfactant should be lower than its critical micelle concentration, in the presence of the silica; but it must be high enough such that it forms a hydrophobic layer around the silica, where the monomer can be adsorbed. The amount to initiator must be low enough to limit the ionic strength to less than 10^{-2}, in order to keep the silica suspension stable. Finally the amount of monomer introduced must remain low at any time and be fully adsorbed onto the surface of silica, which is modified initially by the surfactant and later on by the polymer. Thus a protocol of continuous addition of monomer is used; the total amount of monomer will depend on the final content of silica wanted for the latex. A typical kinetic curve is shown in *Figure 1*; the arrow indicates the end of the monomer addition process.

Two sets of latexes were studied: the first one with non-functionalized silica and the second with functionalized silica. The conditions of their synthesis are given in *Table 1*. The final latexes and samples taken at various times were treated according to *Scheme 2*.

In the case of non-functionalized silica, all the polymer can be dissolved in boiling toluene; there remains silica without any polymer grafted onto it. It can be concluded that, as expected, the polymer is simply adsorbed onto the silica surface. The data concerning the extracted polymer are reported in *Table 2*. These data show that the molecular weight of the polymer increases when the



Scheme 2 Treatment of the latex to separate the encapsulating polymers that are simply adsorbed or grafted

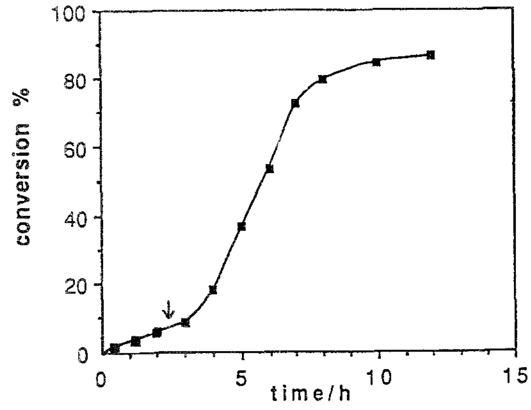


Figure 1 Emulsion polymerization of ethyl acrylate in the presence of 11% (weight percentage of monomer) of MPTMS-functionalized silica. Monomer conversion (%) *versus* polymerization time (h)

amount of silica increases. It follows the common behaviour of emulsion polymerization if one considers the variation in the number of polymer particles. The molecular weight is expected to increase with the number of latex particles due to the longer time interval between the entry of two successive radicals in each particle. On the other hand, the radius of gyration of the polymer extracted from the latex containing silica is definitely smaller than the one of the polymer from the pure latex. The latter, in the absence of silica, was prepared using a batch process; in the presence of silica, a semi-continuous process was used, with monomer-starved conditions. Then more transfer onto the polymer may take place, leading to a more branched structure. In addition, the calculated thickness of polymer around the silica is very small compared to the radius of gyration of the molecules relaxed in a good solvent, so that inside the latex particles the conditions are favourable for grafting onto the polymer.

When MPTMS-functionalized silica is used, a part of the polymer remains on the silica after toluene extraction. The part increases with the amount of silica as shown in the data reported in *Table 3*. The remaining part is quite similar to the polymer extracted from non-functionalized silica, with the same trend in molecular weight *versus* the amount of silica. The polymer shell thickness seems to be very small; a possible reason is the fact that the initial MPTMS-functionalized silica, when dispersed in water, is actually slightly agglomerated. Its diameter is 37 nm, while the diameter of the initial Degussa particles was only 12–13 nm (value also observed in toluene after functionalization). There is interstitial volume inside these particles and the polymer can be partly located in that volume. In addition the formation of the polymer may also dislocate some of these agglomerates, giving smaller particles not well detected by the light scattering apparatus in the presence of larger particles, still agglomerated.

Table 2 Polymer characterization: non-functionalized silica

Silica (wt%)	Weight-average M_w	R_g (nm)	Polymer layer thickness (nm)
0	182 000	48.6	–
3	180 000	35.2	17
6	261 000	36.8	13
11	318 000	50.0	10.5

Table 1 Synthesis of poly(ethyl acrylate) encapsulated silica

Silica	Monomer/silica weight ratio	Conversion (%)	SiO_2 (%)	D_n (nm)	Particle number (10^{16} per litre)	Latex/silica number ratio
NO	–	95	0	76	38	–
NF[a]	32	92.8	3	56	103	4
	16	92.8	6	48	164	3.15
	8	92.6	11	43	227	2.18
F[b]	64	91.6	1.5	74	439	8.60
	16	86.3	6	46	244	1.19
	8	83.5	11	41	387	0.94

[a] Non-functionalized
[b] MPTMS-functionalized

Table 3 Polymer characterization: functionalized silica

	Grafted polymer			Adsorbed polymer			Polymer/shell thickness
Silica (wt%)	(%)	M_w	R_g (nm)	(%)	M_w	R_g (nm)	(nm)
1.5	9	> 24 000	37	87	271 000	55	18.5
6	32	> 25 000	33	60	86 000	41	4.5
11	48	> 29 600	36	40	320 000	49	2

There are questions about the molecular weight of the grafted polymer. After digestion of the silica by HF, the polymers are soluble in toluene and their apparent molecular weight is much lower than for the adsorbed polymer. That method of separation of the grafted polymer has already been used in the literature in the case of polystyrene[2] or poly(methyl methacrylate)[23] and it is claimed that there is no degradation of these polymers in similar experimental conditions. The poly(ethyl acrylate) studied here is much more sensitive to chain scission. When treated at 50°C by concentrated (40 wt%) HF, the molecular weight (M_w) of the polymer prepared in the absence of silica drops from 182 000 to 30 000. If the temperature of the treatment is only room temperature, the final molecular weight is 60 000. Even in these conditions, hydrolysis can be expected. Complete hydrolysis to poly(acrylic acid) does not take place, because the polymer is still soluble in toluene. Partial hydrolysis may account for the observed radius of gyration, rather larger than expected for polyacrylate of moderate molecular weight, and which can be due to possible repulsion of partly dissociated carboxylic groups.

However, whatever the polymer degradation mechanism, the existence of a chemical link between the polymer and the MPTMS-functionalized silica is proved, but the molecular weight of the grafted polymer is not known. But it can be recalled here that, in the case of polystyrene[2] or poly(methyl methacrylate)[23], the molecular weights of both grafted and non-grafted polymers were reported to be the same, and possibly the same conclusion might be valid in the case of poly(ethyl acrylate).

Grafting kinetics of ethyl acrylate polymerization onto MPTMS-modified silica have been studied. The polymerizations have been stopped after a limited time and the polymer characterized. The results, for experiments with 6% of silica for the final product, are illustrated by *Figure 2*. The full curve gives the amount of grafted polymer *versus* time, which increases initially and then levels off. The broken curve shows what percentage of polymer formed at a given time is actually grafted.

From these results it can be concluded that the grafting process takes place early during the polymerization. Comparison of the curves shown in *Figures 1* and *2* indicates that the adsorbed polymer begins to be formed later. Other experiments with 3 and 11% silica confirm that the grafting process occurs at the very beginning of the polymerization. Then we can conclude that the modified silica takes a direct part in the nucleation of the emulsion polymerization. From the surface density of grafted MPTMS molecules onto silica, which is 4.6×10^{-6} mol m^{-2}, and the amount of grafted polymer, an estimate can be made of the average number of monomer units in a grafted polymer molecule between two grafting points, assuming full consumption of the anchored methacrylate units. The estimated value of that number does not exceed 15 monomer units, assuming that the initial silica particles of 37 nm diameter are actually agglomerates of about 20 spheres of 12 nm diameter. It means that the grafted polymer is very near the surface with rather short loops between the grafting points. Owing to the questionable values of the molecular weights of the grafted polymers, it is difficult to estimate the number of grafted polymer chains per particle. Possibly the molecular weight of the grafted polymer does not differ from that of the extracted polymer (adsorbed) as in the cases of poly(methyl methacrylate)[23] and polystyrene[2]. It is certainly larger than the measured value after HF treatment. If both measured values reported in *Table 3* for each sample are considered as reasonable limits, the number of grafted polymer molecules per latex particle can be estimated to be between 20 and 200.

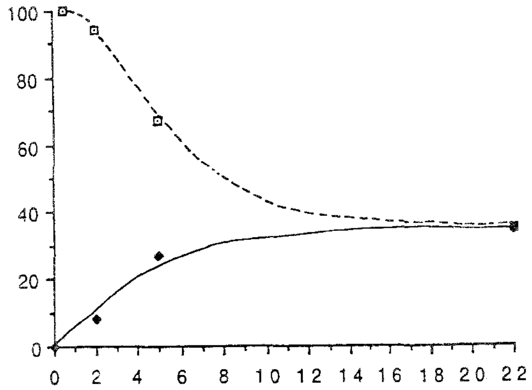


Figure 2 Grafting kinetics of poly(ethyl acrylate) onto MPTMS-functionalized silica (weight ratio monomer/silica = 16/1 (6 wt% silica)). Percentage of grafted polymer *versus* polymer produced (--□--). Kinetics of grafted polymer formation (–◆–)

In several cases, the radius of gyration of the adsorbed polymer (non-grafted) is larger than the particle size, and much larger than the polymer thickness. Indeed the latter was calculated from the difference between the radius of the final latex particles and the initial silica particles. Then the calculated value can be misleading if, due to the polymerization, some disagglomeration takes place (this should be especially significant in the case of functionalized silica). Anyway, it is obvious that these adsorbed polymer molecules are highly compressed inside the final particles. Owing to this highly compressed state, they are expected to be strongly entangled between themselves and also inside the loops of the graft polymer near the silica surface. A schematic picture of such a situation is shown in *Figure 3*.

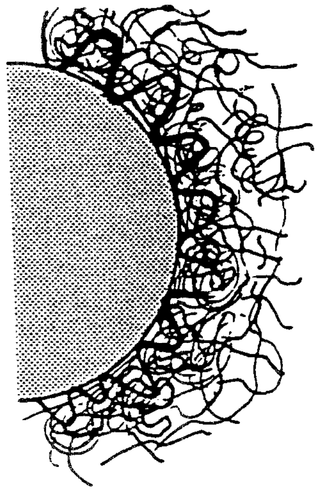


Figure 3 Schematic representation of polymer around a silica particle: loops of grafted polymer are shown as thick lines attached to the silica, and non-grafted polymer chains are shown as thin lines

These compressed conformations seem to be quite a common situation in emulsion polymerization. It has been shown recently by Sperling *et al.*[24], from small-angle neutron scattering experiments, that high-molecular-weight polymer molecules in latex show an apparent radius of gyration much smaller than the actual one. The scattered intensity is much higher than expected and the apparent molecular weight may be up to 10 times higher than the value measured by s.e.c. analysis.

CONCLUSION

Functionalization of silica surface with groups reactive in radical polymerization is needed for actual covalent grafting of polymer onto the silica surface, when emulsion polymerization of ethyl acrylate is carried out in the presence of silica nanoparticles. The grafting process takes place mostly in the early stages of the polymerization. The non-grafted polymer has a high molecular weight, whether or not the silica is functionalized. However, at variance from the cases of polystyrene[2] and poly(methyl methacrylate)[23], nothing can be said about the molecular weight of the grafted polymer, because it is strongly modified by the separation procedure, involving the destruction of the silica with concentrated HF.

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