Functionalization of Silica Particles towards Cationic Polyelectrolytes using Vinylformamide and 1,3-Divinylimidazolidin-2-one as Monomers

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SUMMARY: The use of vinylformamide and 1,3-divinylimidazolidin-2-one**,** bisvinylethylene-urea (BVU), as well as of the poly(vinylformamide–vinylamine) copolymer (PVFA-co-PVAm) for silica surface functionalization has been investigated. Various procedures such as grafting from, crosslinking surface polymerization, and post-functionalization of adsorbed PVAm chains have been experimentally applied. The advantage of the different synthetic methods is discussed with regard to the resulting surface structure of the organic/inorganic hybrid materials.

Introduction

Surface functionalization of inorganic substrates with polyelectrolytes plays an important role in technical application and material science[1-6]. Polyelectrolytes can be linked to polar surfaces of inorganic oxidic particles or flat substrates by different techniques: Either by a grafting from mechanism using covalently immobilized initiators or by consecutive adsorption of oppositely charged polyelectrolytes from water[1-7]. The two established surface structures are illustrated in Chart 1.

Chart 1:   Methods known for surface functionalization of inorganic substrates with
           polyelectrolytes.
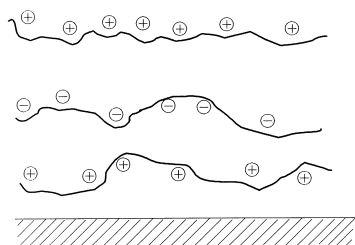
multi layer adsorption of
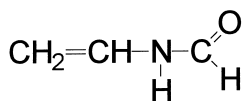oppositely charged polyelectrolytes
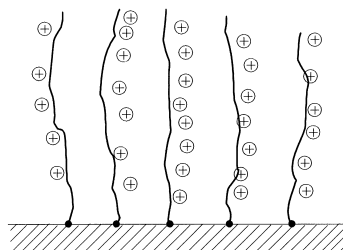
grafted polyelectrolyte brush

Unfortunately, the use of water as solvent for surface functionalization limits the application of the polymers as well as chemical reaction for further derivatization. In this paper we will briefly show some adequate concepts which allow the construction of cationically active polyelectrolytes on silica particles surface. For this purpose, polyvinylamine (PVAm) as polymer has been chosen, because the primary amino groups offer a lot of possibilities for post-functionalizations on the hybrid particles surface. PVAm is synthesized by radically or cationically induced polymerization of vinylformamide and consecutive acid hydrolysis of polyVFA[8-10]. PolyVFA-co-PVAm is a promising polymer, due to the potentiality of controlling the polyelectrolyte properties widely, e.g. by the degree of hydrolysis (content of amino groups) and the pH strength of the aqueous solution (see Chart 2)[6]. The irreversibly linking to silica surfaces can be achieved by three different procedures:
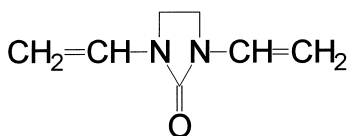
- Grafting from of VFA with an immobilized initiator and hydrolysis of the grafted PVFA
  chains,
- surface crosslinking polymerization of VFA with BVU,
  and hydrolysis of the PVFA sections among the immobilized network, and
- post crosslinking of adsorbed PVFA-co-PVAm with bifunctional reagents (epoxides,
  isocyanates, carbon acid anhydride).

BVU can also be homopolymerized cationically on silica yielding a two-dimensionally ordered crosslinked polyurea network[11]. The use of the poly-BVU/silica hybrid particles for derivatization towards guanidine function is also described in this paper.
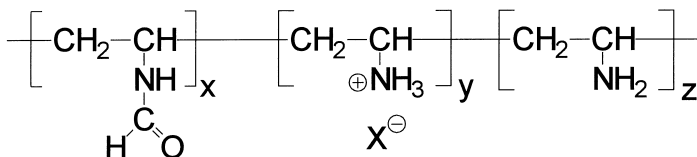
Chart 2: Compounds used for silica functionalization.

$$CH_2{=}CH{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\diagup}}{C}{\diagdown}H$$

VFA

$$CH_2{=}CH{-}\underset{\underset{O}{\parallel}}{N}\quad N{-}CH{=}CH_2$$

BVU

$$\left[CH_2{-}\underset{\underset{\overset{|}{C}}{\underset{\diagdown}{NH}}}{CH}\right]_x \quad \left[CH_2{-}\underset{\oplus NH_3}{CH}\right]_y \quad \left[CH_2{-}\underset{NH_2}{CH}\right]_z$$

$$H \quad O \qquad X^{\ominus}$$

PVFA-co-PVAm

Results and discussion

Grafting from procedure

For the grafting from procedure, we used an azo compound as surface initiator as described by Rühe et al.[7]. This pathway for surface functionalization requires essentially three steps[12,13]:

1. The covalent immobilization of the surface initiator (often additional several steps),

2. the heterogeneously induced grafting from polymerization of the monomer in a slurry, and

3. the hydrolysis of the grafted PVFA chain towards PVAm (see Chart 3).

Of course, after each synthetic step, a purification by extraction is also necessary[7,11-13]. The structure of the surface bonded initiator is evidenced by solid state ^{13}C-CP-TOSS-NMR spectroscopy (Figure 1) and quantitative elemental analysis.

Results for the surface grafting from reaction of VFA with the immobilized azo initiator on silica are given in Table 1.
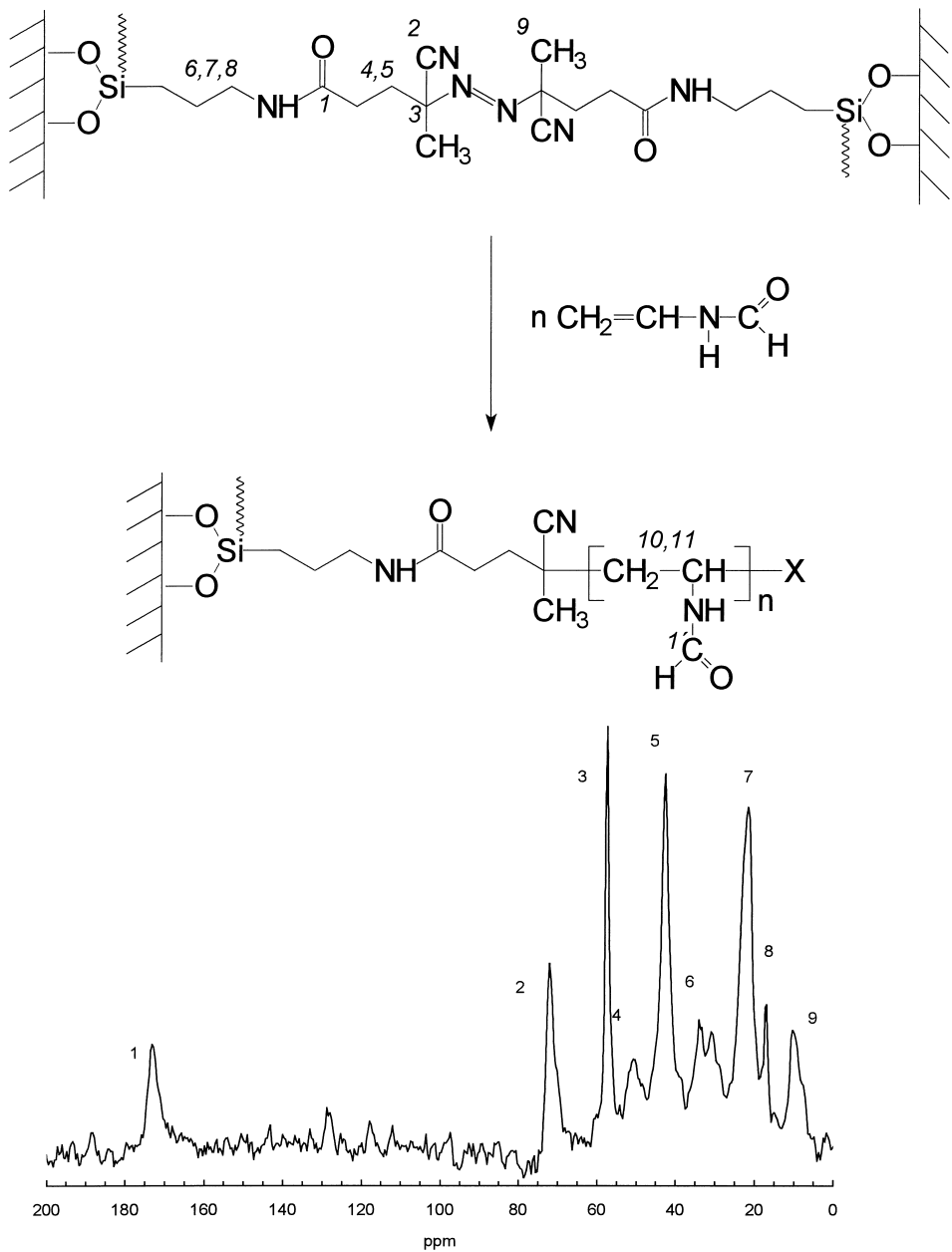
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Chart 3: Crafting from reaction of VFA.

Fig. 1: Solid state $^{13}C\{^{1}H\}$CP-TOSS-NMR spectrum of the azoinitiator immobilized on a silica gel.

Table 1. Grafting yield and monomer conversion for the grafting from reaction of VFA with immobilized azo initiator on silica. T = 338.15 K.

solvent	methanol	ethanol	benzene	toluene	water
reaction time (h)	24	24	24	24	24
conversion VFA (%)	34	34	70	95	100
graft density (g polym./g silica)	0.2044	0.2057	0.2458	0.2770	0.1449

Unfortunately, PVAm is only soluble in water and, therefore, the PVFA formed during the grafting reactions in organic solvents adsorbs very strongly on the particle surface and limits the grafting reaction molecular weight and monomer conversion. In water, the monomer conversion is complete, but then the solution polymerization is preferred, because one part of the azo initiator initiates the solution polymerization which proceeds very well in water. In conclusion, the grafting from method is suitable for PVFA functionalization of silica but not very effective. Figure 2 shows the solid state ^{13}C-CP-TOSS-NMR spectrum of a PVFA/silica hybrid particle sample.
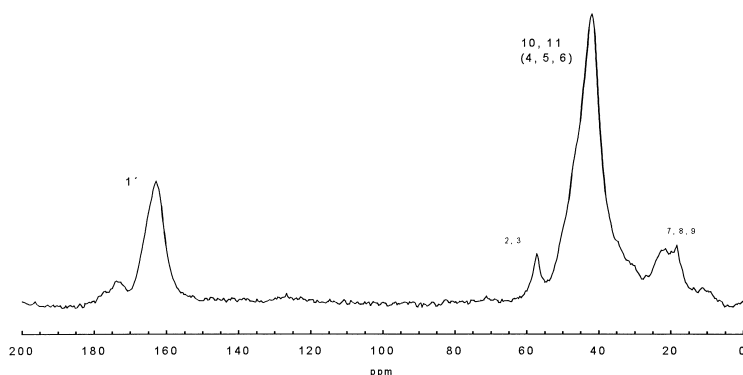

Fig. 2: Solid state ^{13}C{^{1}H}CP-TOSS-NMR spectrum of grafted (from) PVFA on silica. Assignment of the signals see Chart 3.

A second problem results from the instability of the amide bond which links the grafted PVFA-chains to the silica surface, because these bonds can also be cleaved when the formamide groups are acidically hydrolysed to amino groups.

Crosslinking surface polymerization

Cationic homopolymerization of BVU

BVU can be cationically homopolymerized on silica and a crosslinked poly-BVU layer is formed[11].

However, polyurea is not yet a polyelectrolyte, because its basicity is reduced compared to PVAm[14]. But poly-BVU can be used for selective adsorption of metal ions (Co^{2+}, Cu^{2+}, Ag^+, Au^{3+}, Fe^{3+}) which offers a lot of further applications in chromatography and catalysis[14, 15].

An interesting option is the transformation of the urea unit into a guanidine structure, because guanidine is even a stronger base than a primary amine. This synthetic step requires the activation of the urea carbonyl bond with triphosgene[16]. The transformation of the urea moiety into a guanidine was studied with tert. butylamine as the reagent. This is shown in Figure 3 (inset: reaction scheme).
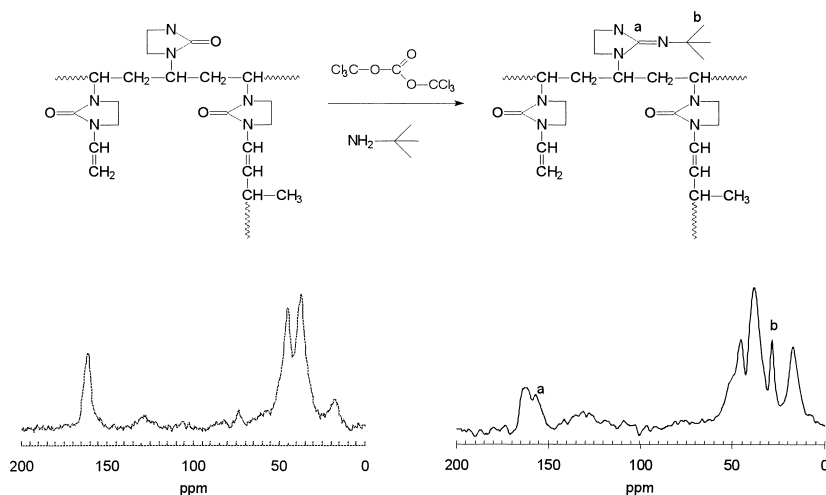

Fig. 3: Solid state ^{13}C-CP-TOSS spectra for guanidine functionalization of poly-BVU network on silica. Inset: reaction scheme.

The introduction of the guanidine is clearly evidenced by the two new signals at δ = 157 ppm and δ = 29 ppm in the solid state ^{13}C{^{1}H}-CP-TOSS-NMR spectrum, relating to the guanidine and methyl groups of the tert. butyl group, respectively. However, this modification reaction proceeds not to a complete conversion of the former urea units despite an excess of the

functionalization reagent triphosgene/tert.butylamine   is used. Other functionalization reactions with Lawessons reagent or reduction with complex hydride compounds have been found not successful for post-derivatization of poly-BVU. .

Radical Copolymerization of VFA with BVU

The target for this functionalization reaction is shown in Chart 4.

Chart 4: Radical surface crosslinking (core shell) polymerization of VFA with BVU on silica particles and hydrolysis to PVAm.
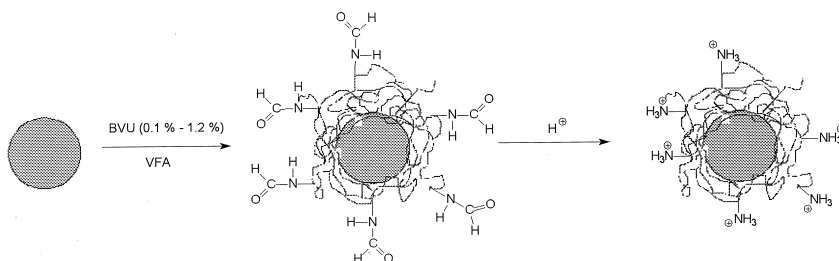

The content of the BVU component significantly determines the morphology of the PVFA-BVU gel formed among the silica matrices. If a concentration of about 1.5 % BVU is used, crosslinking between the silica particles is observed. Details on this reaction and the hydrolysis of the PVFA sections to PVAm will be reported in a following paper[17]. It should be briefly noted that the BVU units remain stable during the acid hydrolysation reaction. Therefore, this method is especially useful for immobilization high amounts of PVAm on silica.

Adsorption of PVAm and post-crosslinking reaction

PVAm can be adsorbed on silica from an aqueous solution[6]. However, the process is significantly dependent on the property of the PVFA-co-PVAm component. Best results (a high amount of PVAm is adsorbed) have been found when a PVAm sample with a high molecular weight (M_n = 400.000 g mol^{-1}) and nearly complete hydrolysis of the former formamide groups (95 %) is used[6]. Surface charges of bare silica and PVAm/silica hybrids have been investigated by zetapotential and surface charge titration[6]. Based on these results, it was concluded that the adsorption energy of PVAm on silica in water is determined by

electrostatic forces rather than by chemical interactions. Consequently, the PVAm layer can be easely removed by competing acids or bases. Irreversibly fixing of the adsorbed PVAm chains can be carried out with different bifunctional reagents, e.g. epoxides, diisocyanates[6], and fulleren molecules[18]. But this is not possible in water which is an essential solvent for PVAm[18]. Therefore, the synthetic concept requires two steps: adsorption of PVAm on silica in water, purification of the pre-functionalized PVAm/silica particles, and then post-functionalization in a suitable organic solvent. The synthetic steps are shown in Chart 5. Figure 4 shows the pH dependent zetapotential plots for bare silica, PVAm/silica, diisiocyanate functionalized PVAm/silica, and C_{60} - functionalized PVAm silica.

Chart 5: Adsorption of PVAm on silica particles and post crosslinking reaction.
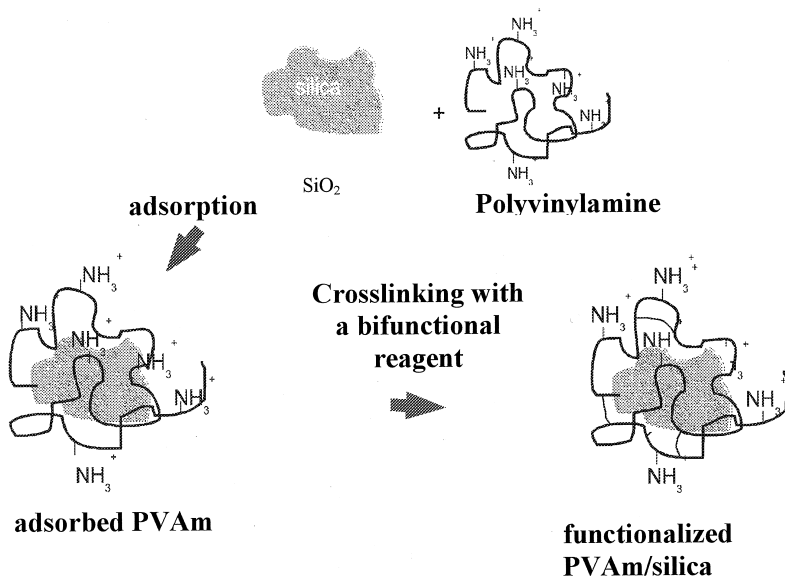
The results in Fig. 4 clearly show that post-functionalization does not disturb the polyelectrolyte properties of the crosslinked PVAm chains. However, a shift of the isoelectric point after post-functionalization to lower pH indicates a conversion of amino groups of the adsorbed PVAm chain.
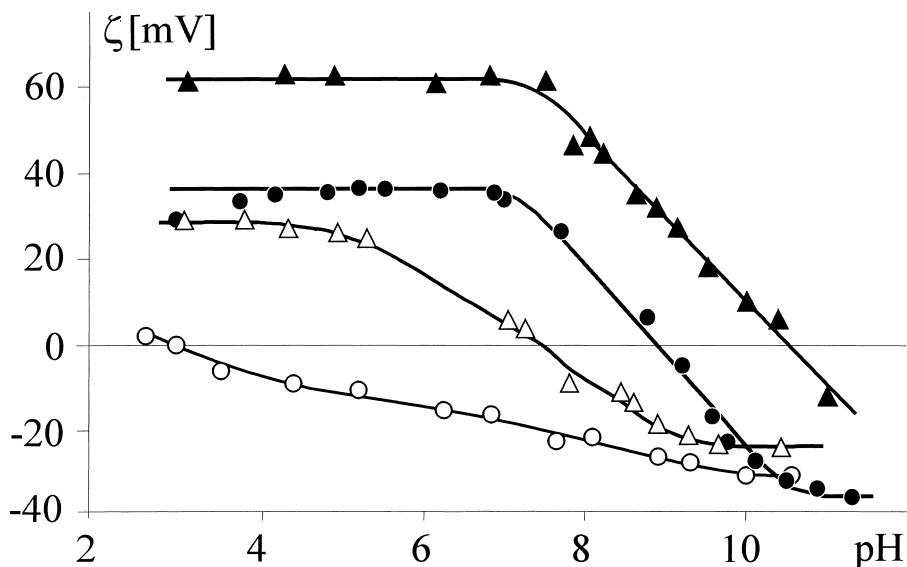
Fig. 4:   Zetapotential as function of the pH for ○ bare silica, ▲ PVFA-*co*-PVAm-95/silica

$(M_n = 400,000 \text{ g·mol}^{-1})$, ● PVFA-*co*-PVAm-95/silica functionalized with 0.10 wt: %

(4,4′-diisocyanate)diphenyl methane, and △ PVFA-*co*-PVAm-95/silica

functionalized with C_{60}. All samples were measured in $1 \cdot 10^{-3}$ mol·l^{-1} KCl at 25 °C[6].

But this effect is not so dramatic compared to bare silica. When PVAm is adsorbed on silica, a shift of the IEP of ΔIEP = 10 is observed. For details see ref.[6] and ref.[18].

Conclusion

Vinylformamide is a very suitable monomer for surface functionalization, because the corresponding polymer which results after surface polymerization can be easely transformed by an acid hydrolysis to PVAm. Grafting from polymerization is possible but not very effective. Crosslinking copolymerization of VFA with BVU on silica is a suitable method. Adsorption of PVAm from water is also possible. This procedure requires a post-derivatization reaction in organic solvent. Experimental details are given in the references[6,11,14, 17, 18].

Acknowledgement

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