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APPLICATION OF CATIONIC POLYMERIZATION TO GRAFTING AND COATING OF SILICA PARTICLES

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Abstract

The cationic polymerization of electron rich monomers such as vinyl ethers, vinyl furane, and cyclopentadiene on silica surfaces can be initiated by aryl methyl halides. The reactions yield always soluble polymers (by heterogeneous catalysis) and novel polymer/silica hybrid materials. The link between polymer and solid is caused by covalent Si-O-C bonds, by network formation of the polymers during the chain growth, or by a combination of both of them. The analysis of the polymer structures on the surface by ^{1}H MAS NMR spectroscopy in suspension and by solid state ^{13}C CP MAS NMR spectroscopy is described. Proof of Si-O-C bonds via DRIFT spectroscopy and ^{13}C CP MAS NMR spectroscopy is given. The most effective method of irreversibly linking the polymer to the silica surface is the network formation. Polyvinyl ethers are bound strongly to the surface, as can be shown by FTIR measurements, but the linkage is not stable due to the Si-O-C bonds' susceptibility to hydrolysis.

Poly-cyclopentadienes (PCPD) are linked to the surface by Si-O-C bonds, which show an extraordinary high resistance to acids and bases. Si-O-C bond formation of poly-2-vinyl furane could not yet be detected by ^{13}C CP MAS NMR spectroscopy and DRIFT spectroscopy. In this case the high degree of coating derives from the bifunctionality of 2-vinyl furane: it may undergo Friedel-Crafts-alkylation at the 5-position of the furane ring as well as chain polymerization via the vinyl group at the 2-position.

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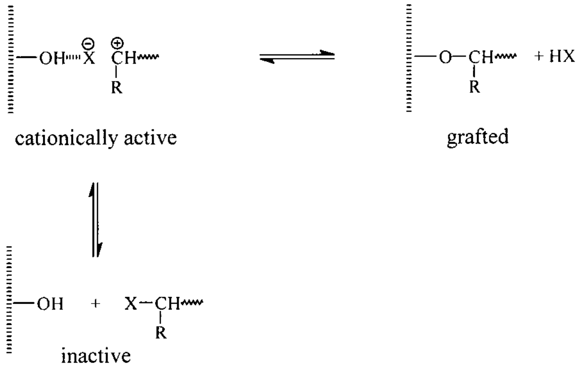
Introduction

The chemical linkage of synthetic organic polymers to inorganic solids, e.g. oxidic fillers or metallic particles, is at present an intensively studied field (Refs.1,2). In order to obtain a strong bondage between the inorganic and organic components it is desirable to introduce covalent bonds to the interface (Ref.3). Polymers may be fixed to the surface by the "grafting from" or the "grafting onto" method (Refs.4,5). Yet, both methods have their disadvantages. The steric demand of the surface adsorbed macromolecule causes incomplete conversion of the polymer end groups ("grafting onto"). In the "grafting from" method the initiator must be introduced to the surface in one or several steps which means complex synthetic procedures (Ref.4). Thus, it is desirable to find a method which allows the modification and polymerization in a single step process.

Up to now we used a method which makes sure that the cationic polymerization of vinyl monomers at silica particles occurs exclusively at the surface of the inorganic component (Refs.5-8). Our mechanistic concept was a ion pair mechanism at the silica surface. This was supported by adsorption experiments with low molecular weight model compounds and Zeta potential measurements (Refs.9–11).The coordination of the growing, cationically active chains to the surface silanol groups is mediated by a nucleophilic counter ion:

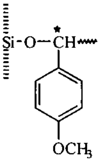
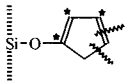
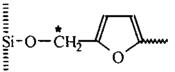
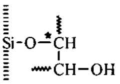
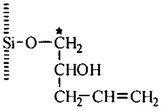
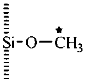


(1)

Thus, the formation of covalent ≡Si-O-CHR~ bonds can be expected and an easy method for the covalent bonding of polymers to the silica particles seems possible (Ref.12). The disadvantage of Si-O-C bonds is their susceptibility to hydrolysis, mainly to acids. This can be minimized if the Si-O-C bond is shielded by hydrophobic groups or by polymer coils (Ref.13).

We observed that during the cationic polymerization of different monomers a part of the polymer remains on the surface. The other part was obtained as soluble fraction (Ref.14). In this work we shall discuss how polymer/silica composites can be obtained and how their features depend on the monomer structure, the initiator structure, and the reaction conditions, and which monomers and initiators are suitable or not suitable for the modification of silica particles. The existence of covalent Si-O-C bonds at silica-polymer composites has been proved by FTIR spectroscopy and solid state ^{13}C NMR spectroscopy (Refs.15,16). A compilation of Si-O-C valence vibrations and ^{13}C shifts of modified silica particles from recent results and from the literature is given in Table 1.

Table 1: Assignment of FTIR and solid state ^{13}C NMR spectroscopy data to covalent Si-O-C bonds at the polymer-silica interface (1–4) and from model compounds (5, 6)

Example	Surface group	$^{13}C^*$ signal [ppm]	Si-O-C* valence vibration [cm^{-1}]	Ref.
1		66.33 (Ref.6)	953.5 (Ref.9)	(6,9)
2		60–80	not detectable	(17)
3		not detectable	964	(18)
4		75,3	957	(15)
5	 $Si{-}O{-}\overset{*}{C}H_2{-}CHOH{-}CH_2{-}CH{=}CH_2$	not reported	960	(16)
6	 $Si{-}O{-}\overset{*}{C}H_3$	50	not reported	(19)

In some special cases the results of the ^{13}C NMR spectroscopy and of the FTIR spectroscopy contradict each other with regard to the existence of Si-O-C bonds. Thus, we shall also discuss the problems of the analytic investigation of cationically generated polymer/silica Si-O-C bonds.

Results and discussion

The monomer – silica interaction

The monomers that have been used so far for the cationic polymerization at silica surfaces are compiled in Table 2. We found that the polymerization reaction is initiated by pure silica only in a few cases. The mechanism, e.g. for methylcyclopentadiene, is still uncertain.

Table 2: Initiation of cationic polymerization of various vinyl monomers induced by bare silica and by the combination silica/tritylchloride in suspension of 1,2-dichloroethane

Monomer	N a)	Silica used		Silica/$(C_6H_5)_3CCl$	
		Aerosil	KG60	Aerosil b)	KG60
N-Vinylcarbazole		–	–	+	+
Ethylvinylether	5.2	–	(+)	+	+
Cyclopentadiene	1.9	–	–	+	+
Styrene	0.8	–	–	+	+
p-Methoxystyrene	3.3 e)	–	–	+	+
Methylcyclopentadiene	3.4 d)	+	+	+	+
2-Vinylfurane	3.8 c)	–	–	+	+
Isobutene	1	–	–	–	–

a) Nucleophilicity parameter, (acc. to Mayr (Ref.20)
b) at –78°C; no polymer is produced
c) Nucleophilicity parameter of 2-methyl furane
d) estimated (Ref.20)
e) H.Mayr, private communication

– no polymerization within 24 h
\+ polymerization occurs

We presume that the monomer (No. 1–4 in table 2) is being physisorbed via the silanol groups. For highly reactive monomers (p-CH_3O-styrene, vinyl ethers) protonation reactions are to be expected, depending on the surface acidity.

The initiator – silica interaction

We used mainly aryl methyl halides as initiators, because they contain $R^1R^2R^3C$-X bonds which can be easily activated by silica. Favourable anions are $X^- = Cl^-$ and $X^- = Br^-$ combined with a cation $R^1R^2R^3C^+$ with a pK_{R+} value in the range of –8 to –4 (Ref.20). Particularly effective initiators of the polymerization at silica are bis-(4-methoxyphenyl)methylium (BMM^+)(pK_{R+} = –5.9) and triphenyl methylium (pK_{R+} = –6.1). Infrared investigations suggest that only a very small fraction of the Si-OH groups react with the initiator (Ref.9).

We succeeded in investigating the Aerosil suspensions directly by ^1H MAS NMR spectroscopy. We found that after the adsorption of BMMCl on Aerosil the silanol protons (signal at 2.4 ppm) could not be detected in the MAS spectrum. Yet, the Aerosil suspension dinstinctly showed the red colour (λ = 510 nm) of BMM^+ (Ref.11) (Figure 1).

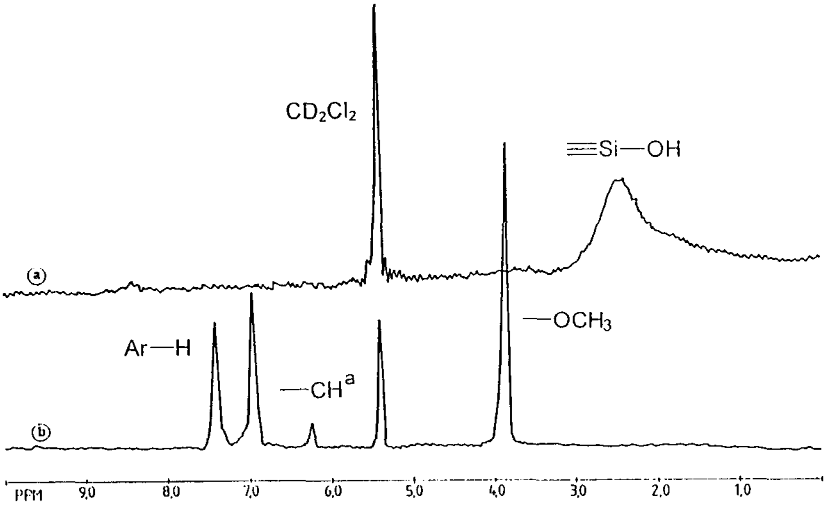
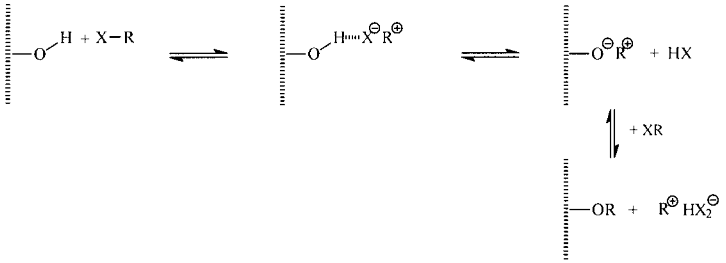
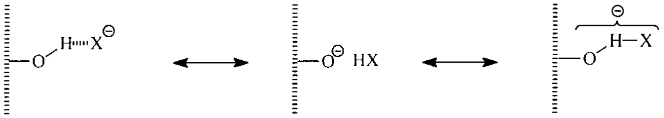


Figure 1: ^1H MAS NMR spectra of Aerosil in CD_2Cl_2 (A), and after addition of BMMCl (B) (rotary frequency 1000 Hz)

This result suggests that the protons either undergo exchange very quickly or are converted directly in a chemical reaction.

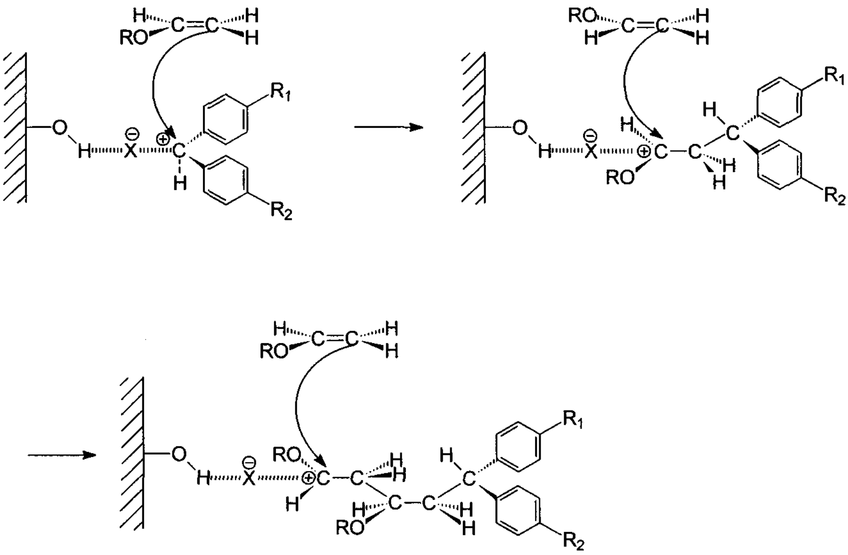

(2)

Is it a rapid equilibrium in which different canonic structures (3) contribute to the stabilization of the bonds of a surface species, or does a reaction according to eq.2 occur? Both approaches are examined at the moment and will be considered in the discussion of the results.


(3)

Polymerization of IBVE on silica

The cationic polymerization of ethyl vinyl ether, isobutyl vinyl ether, and cyclohexyl vinyl ether yields mainly a fraction of soluble polymer (about 90 % with regard to starting amount of monomer) besides polymer coated silica[21]. If Cl^- is used as counter ion, the content of head groups in the soluble fraction is high. We propose the following reaction pathway:



The degree of surface grafting was determined by carbon elemental analysis of the modified particles. It depends on the monomer/initiator ratio as well as on the monomer/silica ratio in a characteristic manner. The dependency is given in Fig. 2. Similar dependencies with similar degrees of coating were also found with the cationic polymerization of p-methoxy styrene at Aerosil (Ref.3).

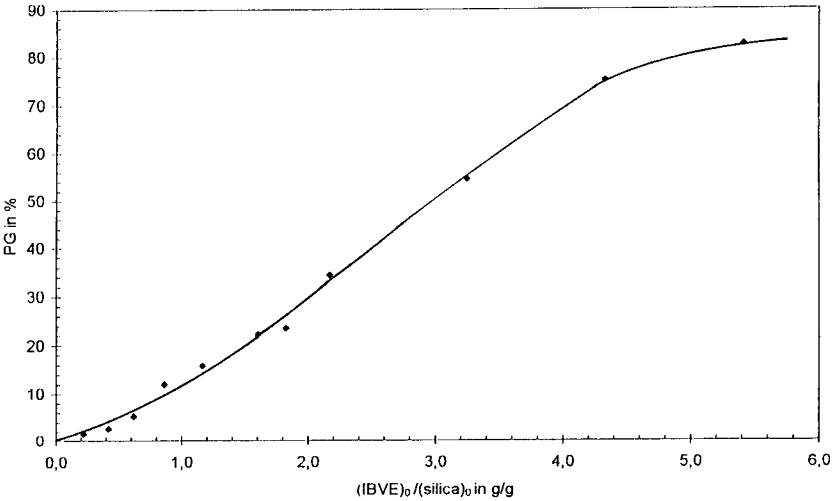


Fig. 2: Degree of grafting (PG) of the composites as a function of the [monomer]/[silica] ratio. System: triphenyl methyl chloride / Aerosil; T = 0 °C; $m_{Aerosil} = 0.5$ g; $n_{initiator} = 1.08 \cdot 10^{-4}$ mol PG = amount of polymer / amount of silica x 100 [%]

The DRIFT spectrum of a PIBVE/silica hybrid material (12.5% C) shows the expected typical new signals for PIBVE besides the signals derived from the original silica surface. The signal of the free silanol groups on the original silica surface at 3746 cm^{-1} is only a weak shoulder in the spectrum of the composite. The broad signals of the water associated Si-OH groups at 3417 cm^{-1} are shifted to 3310.5 cm^{-1} in the spectrum of the composite. This clearly suggests a coordination of PIBVE to ≡Si-OH surface groups. A new, comparatively broad absorption at 967.8 cm^{-1} is observed pointing to a ≡Si-O-CHOR~ valence vibration which is expected at 960 cm^{-1}.

The ^{29}Si {^{1}H} CP MAS NMR spectrum of the PIBVE/silica hybrid shows a broad signal at -100 ppm, where the originally resolved signals of geminal silanol bridges (Q2), isolated silanol groups (Q3), and siloxan bridges (Q4) of the initial silica gel had been (Fig.3).

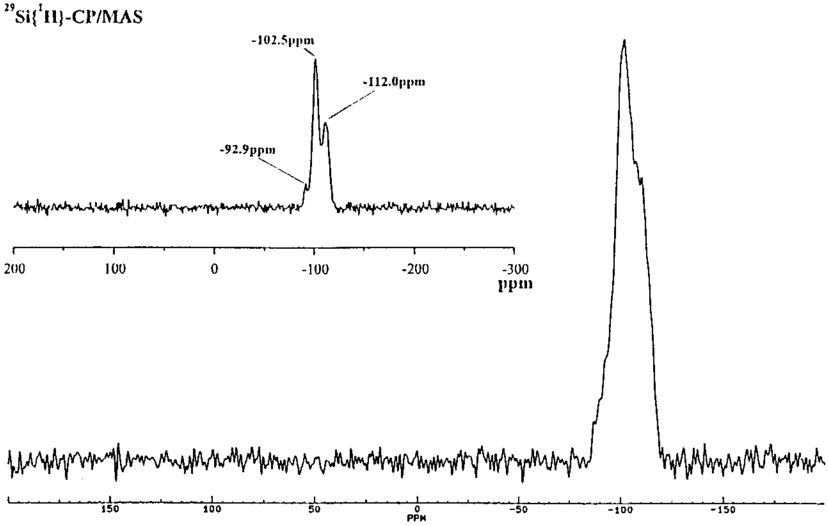


Fig.3: ^{29}Si {^{1}H} CP MAS NMR spectrum of a PIBVE Aerosil adsorbate compared to a spectrum of pure Aerosil

This result also suggests a strong but unspecific interaction of PIBVE with the silica surface. It seems as if the Si-OH and Si-O-Si bonds were changed by the surface polymerization. ^{29}Si signals indicating Si-O-C bonds are not observed. To sum up, it can be said that vinyl ethers can be fixed cationically onto silica, but that the bonds are not stable towards acids, bases, and organic solvents.

Polymerization of vinyl furane on silica

The cationic polymerization of 2-vinyl furane on silica, with $(C_6H_5)_3CCl$ as initiator, yields coloured polymer/silica hybrid materials. The formation of the product is influenced strongly by the reaction temperature. At room temperature the reaction runs comparatively fast, yielding deep blue coloured silica particles. Different colours are obtained at deeper temperatures (< –40 °C). The degree of grafting can be adjusted by varying the usual parameters (i.e. amount of monomer, amount of silica, reaction temperature).The bifunctional properties of the monomer result in the formation of a polymer network on the surface: vinyl furanes possess two π-nucleophilic sites which may both be attacked by electrophils. The reactivity of those sites is about the same, with a slight preference of the 5-position of the furane ring. An alkylation percentage of the 5-position below 50% could not be observed in a single case. Fig. 4 shows a typical ^{1}H NMR spectrum which was taken directly during the vinyl furane polymerization on Aerosil in $CDCl_3$ with an assignment of a part of the signals of the poly-vinyl furane network.

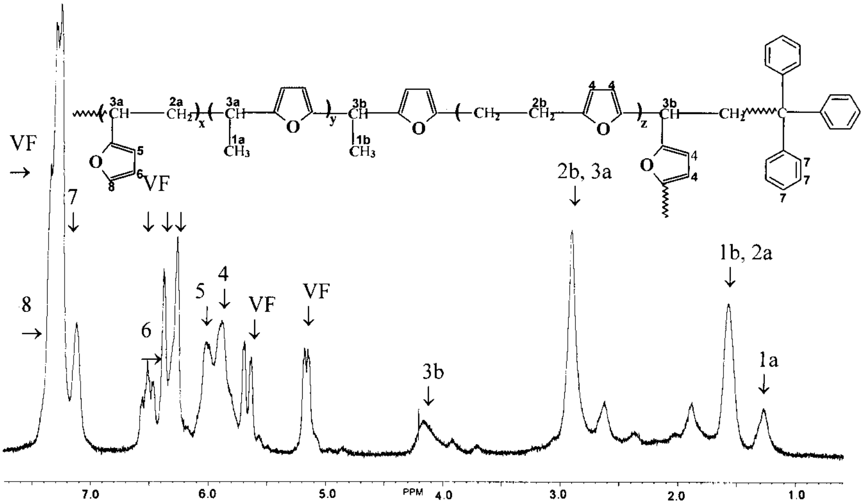


Figure 4: ^{1}H NMR spectrum of a suspension of Aerosil 380/$(C_6H_5)_3CCl$/2-vinyl furane in $CDCl_3$ after 26 h (−20°C, 30 mg Aerosil to 1 ml of the solvent)

The colour of the poly-vinyl furane/silica particles derives from conjugated sequences in the polymer. We attribute the formation of these seqences to a hydride ion transfer reaction from the formed polymer to surplus triphenyl methylium initiator. When the experiment is carried through with a low monomer/initiator ratio, triphenyl methane is found in the reaction mixture and the formation of the coloured particles is considerably faster.

The polymerization of cyclopentadiene on silica

The polymerization of cyclopentadiene on silica can be initiated by $(C_6H_5)_3CCl$, $(C_6H_5)_3CBr$, methyl triflate, or CF_3COOH, yielding PCPD modified particles. They show a deep blue or green colour which results from polyenylium structures. Some characteristic UV spectra are given in Fig. 5.

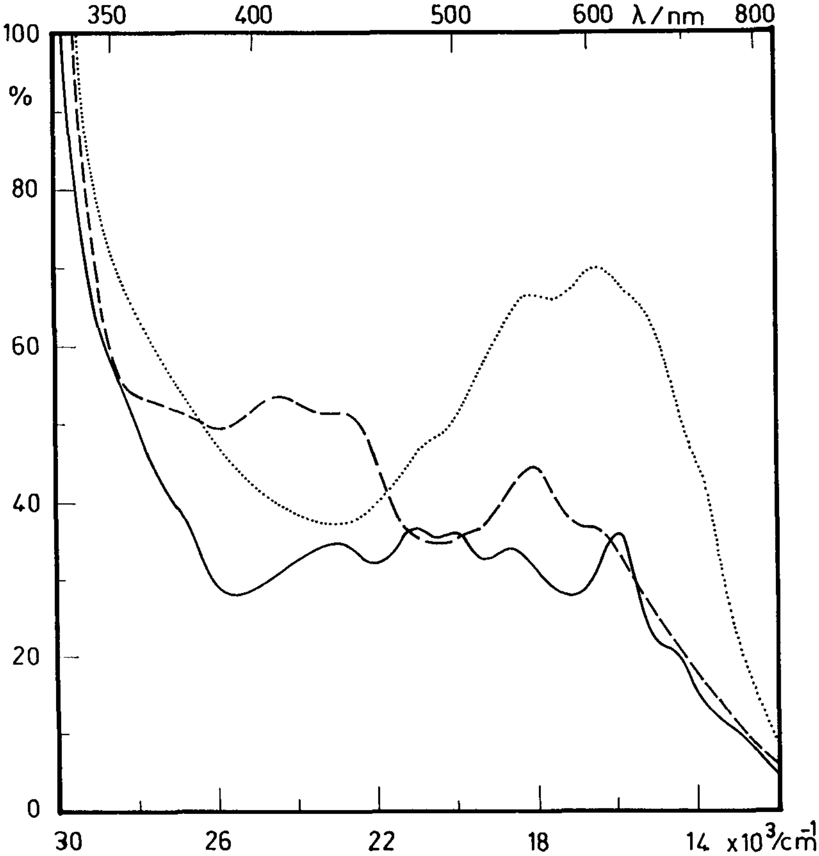


Figure 5: Characteristic UV/VIS spectra obtained after polymerization of CPD in Aerosil/1,2-dichloroethane suspension

---- Aerosil = 0.5 g; CPD = 0.16 mol L^{-1}; $(C_6H_5)_3CCl = 7.2 \cdot 10^{-3}$ mol L^{-1}

······ Aerosil = 1.0 g; CPD = 0.03 mol L^{-1}; $(C_6H_5)_3CBr = 7.7 \cdot 10^{-4}$ mol L^{-1}

— Aerosil = 0.5 g; CPD = 0.009 mol L^{-1}; $CH_3OSO_2CF_3 = 4.6 \cdot 10^{-3}$ mol L^{-1}

The formation of the polyenylium structures is a very complex process which has been discussed in Ref. 17. The polyenylium structures are linked strongly onto the silica surface. After treatment with methanol and extraction an irreversibly linked part of PCPD remains on the particles. This share can be adjusted to 1% – 25% by variation of the amounts of monomer and initiator, the kind of initiator, or the reaction temperature4).

The strong linkage of PCPD on the silica surface derives from covalent Si-O-C bonds which are astoundingly stable towards hydrolytic attacks. Apart from covalent bonds a low share of new structures can be found. Proof of covalent Si-O-C bonds was produced by $^{13}C\ \{^{1}H\}$ CP MAS NMR spectroscopy. In a typical ^{13}C NMR spectrum the signals of covalent Si-O-C* structures appear between 70 to 90 ppm.17) The broad signals in the spectrum indicate that the polymer structure on the silica surface is not uniform, which restricts the use of the CPD polymerization for special surface modifications. Yet, the low price and the easy availability of CPD renders the PCPD-modified silica particles interesting as filling material or as educt for further modification, e.g. with maleic acid anhydride.

Because of the polyene structures of the PCPD layer the modified surface has a comparatively low ionisation potential of $I_p = 7.9 \pm 0.1$ eV which is the reason for charge transfer interactions with aromates and π-acceptors.

Summary and outlook

The cationic polymerization of electron rich monomers such as vinyl ethers, cyclopentadiene, or 2-vinyl furane on silica particles can be used as method for silica surface modifications. An irreversible and thus stable linkage of the polymer to the surface is achieved by the formation of covalent Si-O-C bonds and of polymer networks on the surface. The reaction conditions must be optimized for every single monomer/initiator/silica combination in order to obtain satisfactory grafting or coating degrees.

As the best method for the investigation of the bonding conditions at the polymer/silica interface has proved to be NMR spectroscopy of the reaction suspensions and of the solid products. A combination of different techniques, here: solution state CP MAS NMR spectroscopy and FTIR spectroscopy has proved to be inevitable.

Acknowledgements

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