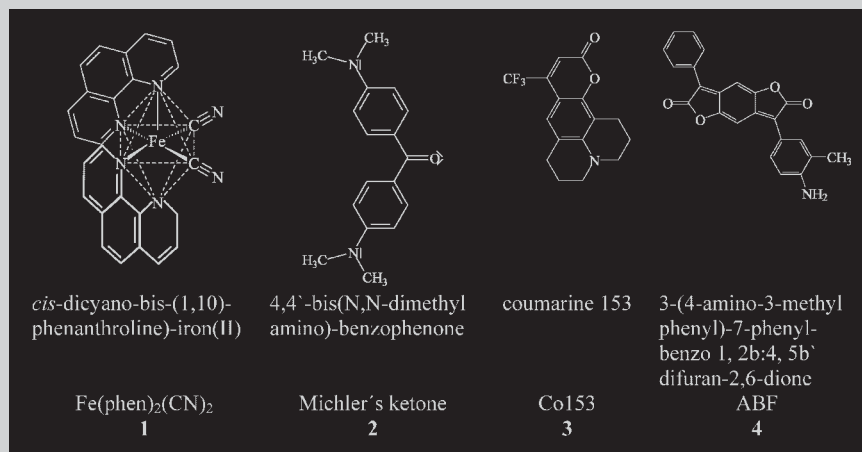**Summary:** The surface polarity of dimethylsiloxane-grafted silica particles (DMS/silica) has been studied as a function of surface coverage by measuring the UV/Vis spectra of coadsorbed solvatochromic probes. Fe(phen)$_2$(CN)$_2$ [*cis*-dicyano-bis-(1,10)-phenanthroline-iron(II), (**1**)] Michler's ketone [4,4′-bis(*N*,*N*-dimethylamino)-benzophenone, (**2**)], coumarine 153 (**3**) and 3-(4-amino-3-methylphenyl)-7-phenylbenzo[1,2*b*:4,5*b*′]difuran-2,6-dione (**4**) were used as solvatochromic surface polarity indicators. Kamlet–Taft's α (hydrogen bond acidity), β (hydrogen bond basicity), and π^* (dipolarity/polarizability) parameters of the DMS/solid acid

interfaces were calculated using different LSE relationships of $\tilde{\nu}_{max}$ data sets of the probes **1** and **2** or **3** (for α and π^*) as well as **1** and **4** (for β). The values for α decrease significantly with increasing conversion of silanol groups with grafted DMS chains. Then, α asymptotically approachs a constant value when more than about 75% of the residual silanols on the surface are grafted with DMS when measured in 1,2-dichloroethane slurry. The π^* values of DMS/silica solvent interfaces seems unaffected by the degree of surface functionalization. The β values of DMS and grafted DMS/silica are clearly lower than the values for α and π^*.

Solvatochromic probes used for the study of the surface polarity of dimethylsiloxane-grafted silica particles.

Surface Polarity of Dimethylsiloxane-Grafted Silica Particles

Silvio Prause,[1] *Stefan Spange,*[1] *Herbert Barthel*[2]

[1] Department of Polymer Chemistry, Institute of Chemistry, Chemnitz University of Technology, Straße der Nationen 62, 09107 Chemnitz, Germany
 Fax: (+49) 371 531 1642; E-mail: stefan.spange@chemie.tu-chemnitz.de
[2] Wacker-Chemie-GmbH, Burghausen, Germany

Introduction

Polydimethylsiloxane (PDMS) and oligodimethylsiloxane (ODMS) are important technical products for silica surface functionalization to improve the compatibility of silica with other polymers in composite and hybrid material synthesis.[1−19] It is not possible to refer to all literature in this

work. For reviews see references [9,10,14,15] and citations therein.

The adsorption of PDMS and ODMS on silica is associated with reaction of reactive chain ends [∼Si(CH$_3$)$_2$–OH or ∼Si(CH$_3$)$_2$–Cl] with surface silanol groups according to a grafting-onto procedure.[1−23] However, the reaction of silanol groups of the silica component with PDMS has been

(a)

(b)

(a)

(b)
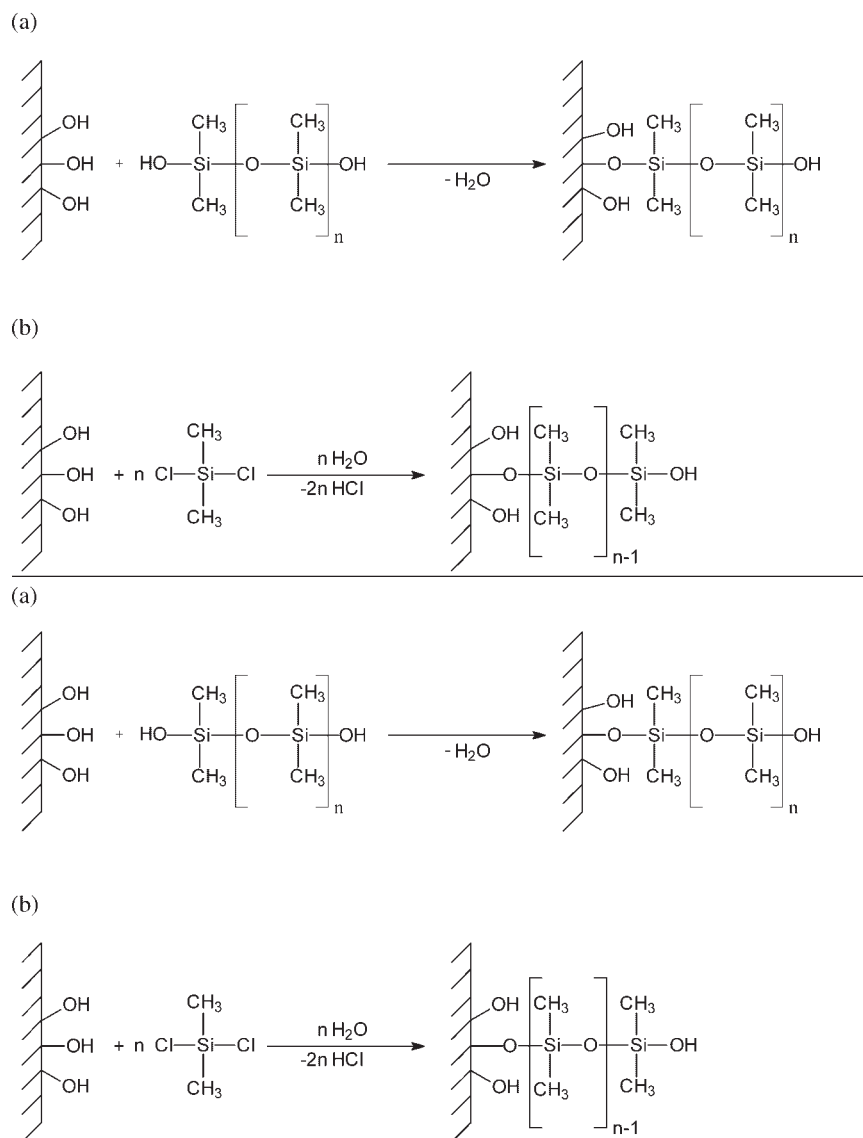
Scheme 1. Surface functionalization of silica with DMS: a) covalent grafting of adsorbed DMS chains; b) surface grafting of silica with dimethyldichlorosilane.

mainly carried out in the melt or during a sol–gel process.[10,12]

Covalent immobilization of dimethylsiloxane (DMS) or ODMS chains can be also achieved by direct surface reaction of dichlorodimethylsilane with silica particles according to a grafting-from procedure.[18,20,21]
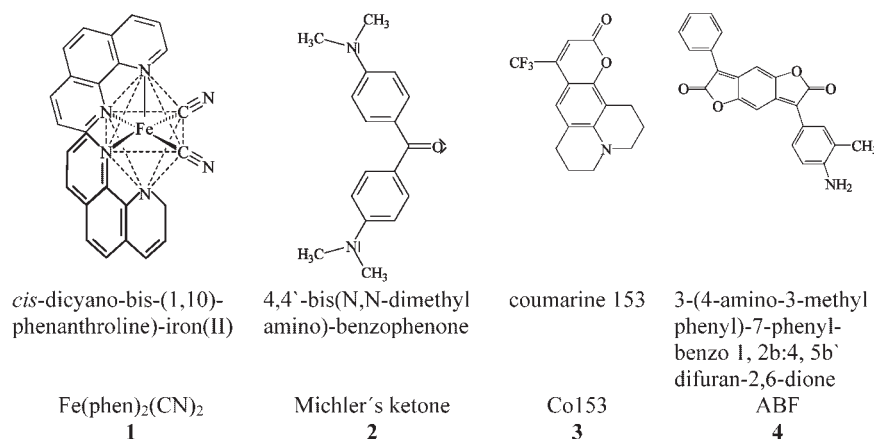
The two ways applied to surface functionalization of silica particles with DMS are shown in Scheme 1.

Compatibility of composite and hybrid materials with either organic polymers or inorganic components (ceramics, metal) is determined, among others, by strong adhesion between the individual components. The forces can be classified in terms of acid–base and nonspecific interactions and can be measured by IGC (inverse gas chromatography) using specific probe molecules.[18] Contact angle

measurements have been also used to investigate surface polarity of DMS/silica hybrid materials obtained by sol–gel techniques.[20]

In this work we make use of solvatochromic probes in order to determine "surface polarity" of DMS-grafted silica in a slurry of moderately polar and nonpolar organic solvents. The probes should serve as models for technical products to understand the influence of the size of functional groups, for example, aromatic polyesters, amines, epoxides, among other parameters, on the compatibility with DMS/silica.

The interaction of a surface environment with a solvatochromic dye is a complex result of many effects.[22,23] Acid–base, dipole–dipole, dipole-induced dipole, and dispersion forces contribute to the overall adsorption

cis-dicyano-bis-(1,10)-
phenanthroline)-iron(II)

4,4`-bis(N,N-dimethyl
amino)-benzophenone

coumarine 153

3-(4-amino-3-methyl
phenyl)-7-phenyl-
benzo 1, 2b:4, 5b`
difuran-2,6-dione

Fe(phen)$_2$(CN)$_2$
1

Michler´s ketone
2

Co153
3

ABF
4

Scheme 2.   Solvatochromic probes used for this study.

energy of a probe with an inorganic surface. This means that for each UV/Vis spectrum of an adsorbed solvatochromic dye measured, surface sites of different polarity as well as different contributions of specific (acid–base) and non-specific (dipolarity/polarizability) interactions must be taken into account.

Multiple intermolecular solute/solvent interactions can be described by the LSE (linear solvation energy) relationship of Kamlet and Taft.[24] The simplified Kamlet–Taft equation applied to single solvatochromic shifts, $XYZ = \tilde{v}_{max}$(probe),[23,24] is given in Equation (1).

$$XYZ = (XYZ)_o + a\alpha + b\beta + s(\pi^* + d\delta) \quad (1)$$

$(XYZ)_o$ is the solute property of a reference system, for example, a nonpolar medium, α describes the HBD (hydrogen bond donating) acidity, β the HBA (hydrogen bond accepting) ability, and π^* the dipolarity/polarizability of the solvents. δ is a polarizability correction term which is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents; a, b, s, and d are solvent-independent correlation coefficients.[23,24]

In this paper, we employ the established UV/Vis spectroscopic method suitable for simultaneously examining the surface acidity α and the dipolarity/polarizability π^* of moderately strong solid organic acids by means of the two surface polarity indicators *cis*-dicyano-bis(1,10)-phenanthroline iron(II) [Fe(phen)$_2$(CN)$_2$, (**1**)] and 4,4´-bis(*N,N*-dimethylamino)benzophenone (Michler's Ketone, (**2**)).[25,26]

Coumarine 153 (**3**) has been also recommended by several authors as a sensitive solvatochromic probe[27] in silica hybrid materials[28] and for investigating preferential HBD solvation.[29] The solvatochromism of **3** responds to the dipolarity/polarizability and HBD capacity of an environment. Its applicability for determining surface polarity and preferential adsorption on HBD sites of DMS/silica will be checked.

As β indicator, [3-(4-amino-3-methylphenyl)-7-phenyl-benzo[1,2*b*:4,5*b*′]difuran-2,6-dione] (**4**) was used.[30–32]

The correlation equations for calculation of α, π^* and β are given in the Experimental Part. Altogether, Scheme 2 shows the formulas of the solvatochromic compounds used in this paper.

The objective of this paper is the determination of the empirical surface polarity parameters α, β, and π^* by means of the indicators **1**, **2**, **3**, and **4** for DMS-grafted silica particles which vary in degree of surface functionalization and for the adsorption of ODMS on silica in 1,2-dichloroethane (DCE) and cyclohexane, respectively.

Experimental Part

Chemicals

Dimethylsiloxy-grafted silicas were prepared by reaction of hydrophilic fumed silica (BET surface area 200 m$^2 \cdot$ g^{-1} and particle size 20 nm) with dimethyldichlorosilane (DMDCS). The silylation was performed by spraying the silane as an aerosol onto the stirred and fluidized silica sample. The silica

Table 1.   Chemical composition and physical properties of the DMS-grafted silica particles.

Sample	BET-surface area	content of carbon	content of residual SiOH	surface conversion Γ with DMS
	m^2 g^{-1}	%	%	%
W0	192	0.03	100.0	0.0
W1	188	0.29	90.7	0.9
W2	179	0.53	79.0	1.6
W3	172	0.98	58.7	3.0
W4	163	1.46	39.2	4.5
W5	151	2.08	26.1	6.4
W6	138	2.54	22.5	7.8
W7	115	3.75	17.1	11.6
W8	104	5.03	13.7	15.5
W9	89	6.73	11.0	20.8

was impregnated beforehand by two moles of water per one mole of DMDCS. Variable amounts of silane were used in order to control the DMDCS coverage ratio. The treated silica samples were then dried at 300 °C for 2 h.

The carbon content was determined by quantitative elemental analysis. The corresponding amount of residual silanol groups Si–OH was then calculated according to reference [21].

The physical characteristics and chemical compositions of the DMS/silica particles are given in Table 1.

Fe(phen)$_2$(CN)$_2$ (**1**) was prepared according to Schilt.[33] Michler's ketone (**2**) was purchased from Merck, recrystallized twice from ethanol, and dried over CaH$_2$ before use. Coumarine 153 (**3**) was purchased from Radiant Laser GmbH and used without further purification. The compound 3-(4-amino-3-methylphenyl)-7-phenylbenzo[1,2b:4,5b'] difuran-2,6-dione (**4**) was kindly provided by the BASF, Manchester. The solvents 1,2-dichloroethane (spectroscopic grade) and cyclohexane were purchased from Merck. Both were dried over CaH$_2$, freshly distilled before use, and stored over carefully dried anhydrous alumina.

UV/Vis Measurements

The equipment employed was a UV/Vis spectrometer MCS 400 connected to an immersion cuvette TSM 5A (Zeiss). The measurements of the transparent slurry and of the sedimentation solution are possible in the same cell.

The UV/Vis absorption maxima of the dyes **1** and **2** adsorbed on the solid acid supports were recorded using a special flask which contains the immersion cuvette.[26d]

The solids were heated at 150 °C for 8 h. After cooling to room temperature under dried argon, an amount (0.5 g) was introduced into the measurement cell and immediately suspended in the solution of the probe dye in the same solvent. The following concentrations were used for the probes:

1 in DCE: 5×10^{-3} mol · l^{-1};
2 in cyclohexane: 10^{-3} mol · l^{-1};
3 in cyclohexane: 10^{-4} mol · l^{-1};
4 in cyclohexane: 10^{-4} mol · l^{-1}.

The reproducibility of the UV/Vis spectra of the adsorbed dyes was very good with $\Delta\lambda_{max} \cong 3$ nm. Specific results are discussed in the results part of the work.

The viscous oligomer is used directly for the adsorption experiments because it can be added by a micro-syringe in the measurement cell through a septum. Details of the UV/Vis absorption measurements in the various solid acid/polymer compositions in DCE and cyclohexane relevant to the scientific interpretation are mentioned in the results part.

Determination of the Polarity Parameters

The α and π^* values were calculated by a correlation analysis of the measured UV/Vis absorption maxima $\tilde{v}_{max}$ (in 10^{-3} cm^{-1}) of the dyes **1** and **2**, using the corresponding multiple correlations of α or $\pi^* = $ f $[\tilde{v}_{max}(\mathbf{1})$ and $\tilde{v}_{max}(\mathbf{2})]$ with the Kamlet–Taft solvent parameters as the reference system.[34] The following multiple correlations [Equation (2) and (3)] were used to separate the respective property α or π^* from the

unit of measurement of the $\tilde{v}_{max}$(indicator) for **1** and **2** (n is the number of solvents used, r is the correlation coefficient, and sd is the standard deviation).

$$\alpha = -7.90 + 0.45 \, \tilde{v}_{max}(\mathbf{1}) \times 10^{-3}$$
$$+ 0.02 \, \tilde{v}_{max}(\mathbf{2}) \times 10^{-3} \qquad (2)$$

$n = 34$, $r = 0.95$, sd $= 0.17$

$$\pi^* = 13.89 - 0.251 \, \tilde{v}_{max}(\mathbf{1}) \times 10^{-3}$$
$$- 0.32 \, \tilde{v}_{max}(\mathbf{2}) \times 10^{-3} \qquad (3)$$

$n = 36$, $r = 0.57$, sd $= 0.15$

For the alternative determination of the surface acidity α a recorrelated LSE relationship [Equation (4)] was used derived from the $\tilde{v}_{max}(\mathbf{1})$ values when adsorbed on various solid acids and the calculated parameters α. Data are taken from our previous paper.[35]

$$\tilde{v}_{max}(\mathbf{1}) \cdot 10^{-3} \, [\text{cm}^{-1}] = 16.27 + 2.20\alpha \qquad (4)$$

$n = 33$, $r = 0.99$, sd $= 0.03$

This equation is statistically proved and allows the determination of α values in relation to our previous works without the knowledge of $\tilde{v}_{max}$ data of a second UV/Vis probe like **2**.

Because coumarine 153 adsorbs well on DMS/silica from cyclohexane, its suitability to observe dipolarity/polarizability has been investigated. Then, π^* values can be calculated by Equation (5) which has been determined using $\tilde{v}_{max}(\mathbf{3})$ data from reference [27] [Equation (5)].

$$\tilde{v}_{max}(\mathbf{3}) \times 10^{-3} \, [\text{cm}^{-1}] = 25.63 - 0.91\alpha - 1.92\pi^* \qquad (5)$$

$n = 22$, $r = 0.94$, sd $= 0.30$

For the determination of the β values of DMS/silica, we used **4** as surface polarity indicator because it sufficiently adsorbs on two DMS/silica batches from cyclohexane.

The β values were then calculated by Equation (6).[25a]

$$\beta = 3.06 + 0.17 \, \tilde{v}_{max}(\mathbf{1}) \times 10^{-3} - 0.33 \, \tilde{v}_{max}(\mathbf{4}) \times 10^{-3}$$
$$(6a)$$

$n = 21$; $r = 0.96$; sd $= 0.10$

β can be also calculated from Equation (6b) taken from reference [30] by knowledge of α and π^*.

$$\tilde{v}_{max}(\mathbf{4}) \times 10^{-3} \, [\text{cm}^{-1}] = 18.60 + 0.97\alpha - 2.93\beta - 0.91\pi^*$$
$$(6b)$$

$n = 25$, $r = 1.00$ sd $= 0.12$

Equation (6a) has been established as very suitable tool for determining accurate β values for various synthetic polymers.[25a,31a]

BET Measurements

The BET surface area was measured with nitrogen at 77 K using a Sorptomatik 1900 (Fisons).

Correlation Analyses

The correlation analyses were done with the statistics tool of Microcal Origin version 5,0 SR2 from Microcal Software.

Table 2. UV/Vis absorption maxima of the probes **1**, **2**, **3**, and **4**, respectively, when adsorbed on DMS-grafted silica particles measured in 1,2-dichloroethane (DCE) or cyclohexane.

sample	$\tilde{\nu}_{max}$ (**1**) in DCE	$\tilde{\nu}_{max}$ (**2**) in cyclohexane	$\tilde{\nu}_{max}$ (**3**) in cyclohexane	$\tilde{\nu}_{max}$ (**4**) in cyclohexane
	10^{-3} cm^{-1}	10^{-3} cm^{-1}	10^{-3} cm^{-1}	10^{-3} cm^{-1}
W0	19.02	26.04	22.57	n.m.[a]
W1	18.94	26.04	22.62	18.78
W2	18.9	26.18	22.68	n.m.
W3	18.73	26.25	22.73	n.m.
W4	18.28	26.46	22.88	n.m.
W5	18.08	26.74	22.99	n.m.
W6	17.95	26.74	22.99	n.m.
W7	17.79	26.81	22.99	n.m.
W8	17.76	26.88	22.99	n.m.
W9	17.76	26.88	22.99	17.76

[a] Indicates that a measurable UV/Vis band cannot be utilized.

Results and Discussion

The degree of grafting has been adjusted by the amount ratio of dimethyldichlorosilane to silica used. Surface modification varies from 89% (sample W9) to 9% (sample W1) conversion of surface silanol groups with DMS (denotation of the samples see Table 1).

Using the moderately polar solvent 1,2-dichloroethane, the probes **2**, **3**, and **4**, respectively, adsorb sparingly on the DMS/silica batches. Thus, in the resulting UV/Vis spectrum of the dye measured in the slurry, contributions from both the adsorbed and dissolved fractions are monitored. A complete adsorption of **2**, **3**, and **4** on the DMS/silica batches takes place in cyclohexane. **1** is insoluble in the nonpolar solvent cyclohexane. Thus, 1,2-dichloroethane was used as solvent for **1**.

The UV/Vis spectra of the polarity indicators **1**, **2**, **3**, and **4**, respectively, adsorbed on the DMS/silica particles were recorded after the components were mixed, usually after a standard period of 24 h to achieve equilibrium conditions. The UV/Vis spectroscopic results are summarized in Table 2.

Altogether, an increase in surface modification with covalently grafted DMS chains significantly influences the UV/Vis shift of each coadsorbed polarity indicator, respectively. Generally, the UV/Vis results obtained using the probes **1**, **2**, and **3** indicate a decrease of both the dipolarity/polarizability and HBD capacity with increasing silanol conversion towards grafted DMS chains. The UV/Vis shift of each of the three indicators responds to changes of the α and π^* of an environment. This is shown by a hypsochromic shift of the solvatochromic UV/Vis band of the probes **2** and **3**, and by a bathochromic shift of the UV/Vis band of **1** (see results in Table 2). Compound **1** is a negative solvatochromic compound whereas **2** and **3** are positive solvatochromic compounds.[23]

The sensitivity of the respective solvatochromic UV/Vis shift of the three indicators **1**, **2**, and **3** as function of solvent polarity is indicated by the sum of *a* and *s* according to Equation (1). The ratio *a*/*s* relates to the susceptibility of HBD- to dipolar-induced interactions of the dye with the surface environment. The values for *a* and *s* for **1** and **2** have been taken from reference [34] and for **3** from Equation (5). To gain information on contributions of α and π^* on the
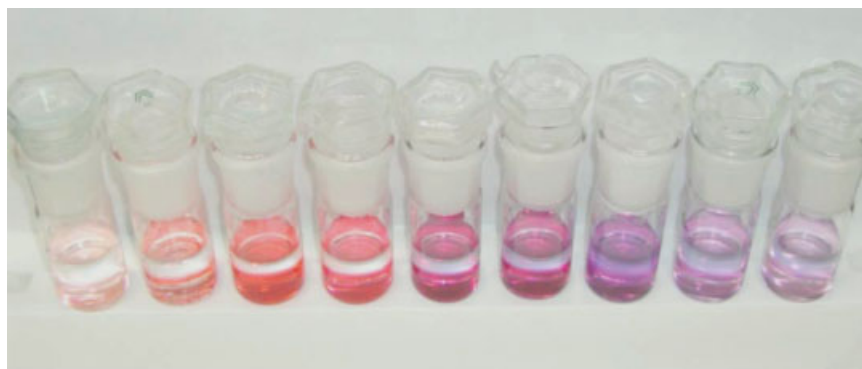

Figure 1. Photograph of Fe(phen)$_2$(CN)$_2$-loaded DMS-grafted silica particles. From left to right, the degree of surface functionalization increases.

extent of the UV/Vis shift, $(a + s)$ and a/s values have been compared with the largest UV/Vis shift ($\Delta\tilde{v}$) observed. $\Delta\tilde{v}$ results from the batches W0 and W9 for each UV/Vis probe.

1: $a = 2.24$, $s = 1.63$; $a/s = 1.37$; $(a + s) = 3.87$, $\Delta\tilde{v} = 1\,260$ cm^{-1}
2: $a = -1.79$, $s = -2.18$; $a/s = 0.82$, $(a + s) = -3.97$; $\Delta\tilde{v} = 840$ cm^{-1}
3: $a = -0.91$, $s = -1.92$; $a/s = 0.47$, $(a + s) = -2.83$; $\Delta\tilde{v} = 360$ cm^{-1}

The outstanding largest UV/Vis shift is observed for the HBD sensitive probe **1** which indicates that HBD (residual silanol) groups mainly determine the surface polarity.

The adsorption of **1** on various DMS/silica batches in DCE can be used as an illustrative experiment for the demonstration of the sensitivity of **1** as a surface HBD acidity indicator. Photograph of **1**-loaded DMS/silica slurries in DCE are shown in Figure 1.

From left to right (sample 1 to 9), the degree of surface functionalization increases, which is indicated by a change of color of adsorbed **1** from red to blue/violet.

It is clear that the larger the a/s ratio, the more sensitively the respective probe observes changes in the surface environment. This is a clear indication that surface functionalization preferentially decreases the HBD capacity, the α term, whereas the π^* term seems weakly affected by surface modification.

According to our previous work, for the calculation of the α and π^* parameters, we utilized $\tilde{v}_{max}(\mathbf{1})$ and $\tilde{v}_{max}(\mathbf{2})$ as well as solely $\tilde{v}_{max}(\mathbf{1})$.[37] The results are given in Table 3.

Plots of α as function of surface coverage Γ (expressed as % conversion of silanol groups), determined from data measured in DCE and cyclohexane, are shown in Figure 2.

α decreases linearly with increasing surface functionalization. This trend is valid up to about 30% conversion of
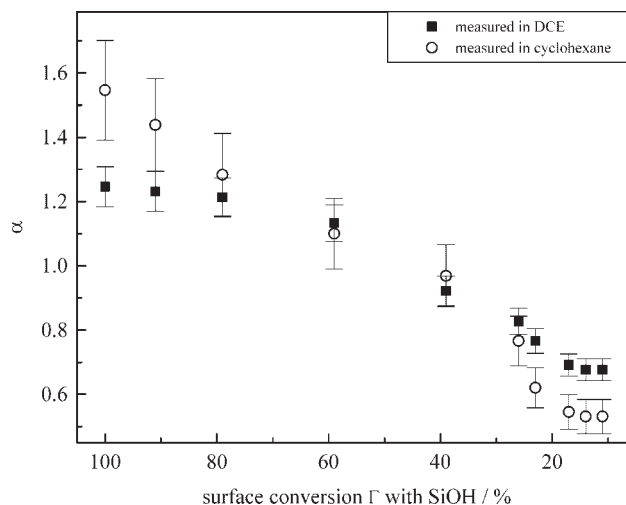

Figure 2. HBD capacity of DMS-grafted silica particles as a function of silanol conversion.

silanol groups [Equation (7a) (in DCE) and (7b) (in cyclohexane)].

$$\alpha = 1.37 - 0.02\Gamma \tag{7a}$$

$$n = 6, r = 0.90, \text{sd} = 0.09$$

$$\alpha = 1.64 - 0.03\Gamma \tag{7b}$$

$$n = 6, r = 0.95, \text{sd} = 0.10$$

Then α asymptotically approachs a constant value. It should be mentioned at this point that adsorbed **3** shows also no UV/Vis shift in this section while **2** observes a continuously small decrease of the overall polarity.

The strength of interaction of Si–OH with the lone electron pair of the cyano group of **1** (NC-**1**) determines the measured α value. Thus, α decreases since either the acidity of the Si–OH group decreases or the distance of the

Table 3. Kamlet–Taft polarity parameters α and π^* of DMS-grafted silica particles calculated by Equation (2)–(5) and the data from Table 2.

Sample	α[a]	π^*[b]	α[c]	π^*[d]
W0	1.18	0.89	1.25	1.00
W1	1.14	0.82	1.23	0.98
W2	1.13	0.79	1.21	0.96
W3	1.05	0.81	1.13	0.97
W4	0.85	0.85	0.92	0.99
W5	0.77	0.81	0.83	0.98
W6	0.71	0.85	0.77	1.01
W7	0.64	0.86	0.69	1.05
W8	0.63	0.85	0.68	1.05
W9	0.63	0.85	0.68	1.05

[a] Calculated from Equation (2).
[b] Calculated from Equation (3).
[c] Calculated from Equation (4).
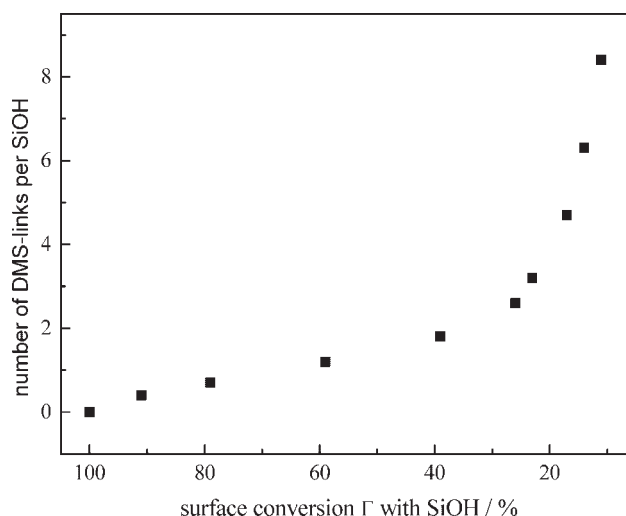[d] Calculated from Equation (5) and α^3.

Figure 3. Average number n of DMS links, [–Si(CH$_3$)$_2$–]$_n$- per Si–OH group, as a function of silanol conversion.

Si–OH. . .NC-**1** coordinative bond increases. IGC measurements with small probe molecules showed that the acidity of silanol groups seems independent of the degree of functionalization from 100% to 40% residual silanols.[18] Accordingly, the decrease of α with increasing surface functionality of grafted DMS is explained in terms that the bulky probe **1** has no direct access to all free silanol groups, because a part of them is sterically shielded by neighboring DMS moieties. The distance between two Si–OH groups on the surface of a fumed silica is about 0.54 nm. This value is evidently smaller than the size of **1** which is in the order of 0.90 nm.[26d] This comparison shows that the steric influence of neighboring DMS groups on the adsorption of **1** on free silanol groups is of great importance. It is also of importance to note that the average length of grafted DMS chains increases abruptly from about 2 to 6 until 8 number (n) of –Si(CH$_3$)$_2$– segments below 30% surface conversion of Si–OH as seen in Figure 3. Average n of [–Si(CH$_3$)$_2$–]$_n$ can be easily calculated from the data in Table 1.

The grafted DMS chains are suitable to form loops with up to 12 to 16 links which are grafted on both sides onto the silica surface. This option is very likely, because free silanol groups deriving from –Si(CH$_3$)$_2$OH groups cannot be detected by infrared spectroscopy. Perhaps, also the DMS/silica particles with low DMS content form greater sized loops, because the elemental analyses allows one to determine the average value of surface functionalization. Therefore, it is possible that the actual number of free silanol groups is greater compared with that determined by elemental analyses. The formation of both side grafted, large DMS loops prevents the interaction of **1** with residual silanol groups more strongly than does the formation of small DMS loops.

As a consequence of the increased loop formation below 30%, surface conversion with Si–OH, $\tilde{v}_{max}$(**1**) and α, respectively, remains really unaffected from 0.5 to 0.2 residual silanol groups per nm^2, because **1** has no access to free silanol groups.

Which influence does the dipolarity/polarizability of the solvent used for the measurement of the HBD capacity play as **1** has been used in DCE ($\pi^* = 0.81$) and the other solvatochromic probes **2**, **3** and **4** in cyclohexane ($\pi^* = 0$). Therefore, we have prepared **1**-loaded DMS/silica samples by preadsorption of **1**. For the systems in cyclohexane, **1** was adsorbed on silica from solution in dichloromethane, and then filtered, washed and dried. The **1**-loaded silica sample was suspended subsequently in cyclohexane and measured as described. Unfortunately, the UV/Vis bands measured of **1** adsorbed on DMS/silica in cyclohexane are broad in some cases and the relevant UV/Vis peak appears as a shoulder in the spectrum which makes the utilization of the relevant $\tilde{v}_{max}$(**1**) data uncertain.

Unprecedented large HBD capacities result for the DMS/silica samples with low grafting density in cyclohexane. α ranges from 1.44 (W1) to 0.53 (W9). These α values are evidently larger than those determined in the slurry in 1,2-dichloroethane. This is an expected result and well in accord to the catalytic activity and HBD capacity of solid acids as function of solvent HBA capacity.[36] Another reason for this result is probably that probe **1** is strongly restricted in its mobility when adsorbed on available silica surface sites, because it is not really solvated by cyclohexane at the interface while DCE does it. We think that the dipolarity/polarizability of DCE preferentially determines the overall surface polarity of the DMS-grafted silica particles from 30 to 90% conversion of silanol groups. That would mean that the dipolarity/polarizability of DCE overcomes the effect of residual silanols and grafted DMS chains in this section. Thus weak HBD capacities of a silica surface ($\alpha < 0.7$) cannot be measured in solvents with $\pi^* > 0.8$.

The π^* values for DMS/silica particles were calculated from Equation (5) and $\tilde{v}_{max}$(**3**) using additionally the independently examined α values from Equation (4). For instance, $\pi^* = 1.00$ for W0 and $\pi^* = 1.05$ for W8 were determined. These values are comparable to the π^* data in Table 2. Therefore, we think that surface dipolarity/polarizability is hardly influenced by grafted DMS chains. This is in agreement with results of a previous paper[26b] which shows that presence of residual silanols and grafted alkyl groups average the dipolarity/polarizability of a surface.

The β sensitive probe **4** could successfully be adsorbed on only two batches (W1 and W8) from cyclohexane. For the other samples, a utilizable UV/Vis spectrum for the determination of β could not be monitored. β of DMS/silica has been determined to $\beta = 0.1$ (for W1) to $\beta = 0.3$ (for W8) which values fit well in the β scale for organic solvents and synthetic polymers.

According to our previous papers,[37] we intended to investigate also the adsorption process of DMS on silica with the coadsorbed solvatochromic probe **1**. However, DMS is a weak HBA polymer. The β value of pure DMS was calculated from Equation (6b) using the $\tilde{v}_{max}$(**4**) = 17.73 $\times$ 10^3 cm^{-1} measured in a DMS film with presumed $\alpha = 0$ and calculated $\pi^* = 0.68$ derived from measured $E_T(30) = 39 \pm 1$ kcal mol^{-1} of pure DMS taken from reference [32c]. The β value of DMS amounts to 0.09. Therefore, the basicity of the indicator **1** or **2** ($\beta_H^2 = 0.65$)[38] as solute is almost larger than that of DMS. As a consequence, DMS adsorption on **1**-loaded silica from a solution in 1,2-dichloroethane does not influence the UV/Vis absorption of the solvatochromic probe.

Conclusion

Surface polarity and HBD capacity of DMS-grafted silica particles as a function of surface coverage can be

investigated by measuring the shift in the UV/Vis absorption band of coadsorbed solvatochromic probes in transparent slurries. The solvatochromic probe serves as an interfacial polarity indicator between the functional surface and the solvent, because the dipolarity of the solvent has a strong influence on the acid–base and dipolar/polarizable interaction of the functional surface with a dipolar probe molecule.[36] The results are of importance to understand the effects of miscibility of DMS-grafted silica particles with nonpolar polymeric or polar inorganic materials in composite synthesis.

[1] M. I. Aranguren, E. Mora, C. W. Macosko, *J. Colloid Interface Sci.* **1997**, *195*, 329.
[2] P. Levresse, D. L. Feke, I. Mans-Zloczower, *Polymer* **1998**, *39*, 3919.
[3] D. W. McCarthy, J. E. Mark, S. J. Clarson, D. W. Schaeffer, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1191.
[4] I. Gill, A. Ballestros, *J. Am. Chem. Soc.* **1998**, *120*, 8587.
[5] T. Sugizaki, M. Oikawa, O. Moriya, T. Kageyama, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2363.
[6] Q. Wendy Yuan, J. E. Mark, *Macromol. Chem. Phys.* **1999**, *200*, 206.
[7] J. M. Breiner, J. E. Mark, G. Beaucage, *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1421.
[8] H. Huang, B. Orler, G. L. Wilkes, *Macromolecules* **1987**, *20*, 1322.
[9] L. Lèger, H. Hervet, M. Deruelle, "Adsorption of Polydimethylsiloxane Chains on Planar Silica Surfaces", in: *Adsorption on Silica Surfaces*, E. Papirer, Ed., *Surfactant Sci. Ser. 90*, Marcel Dekker, New York 2000, 597.
[10] J. P. Cohen Addad, "Adsorption of PDMS on Bare Fumed Silica Surface", in: *Adsorption on Silica Surfaces*, E. Papirer, Ed., *Surfactant Sci. Ser. 90*, Marcel Dekker, New York 2000, 621.
[11] Y. Hu, Y. J. Chung, J. M. McKanzie, *J. Mater. Sci.* **1993**, *27*, 4415.
[12] R. Pena-Alonso, J. Rubio, F. Rubio, J. L. Oteo, *J. Sol-Gel Sci. Technol.* **2002**, *25*, 255.
[13] S. Y. Lu, H. Y. Huang, K. H. Wu, *J. Mater. Res.* **2001**, *16*, 3053.
[14] C. Kumudinie, J. E. Mark, "*Organic/Inorganic Hybrid Materials II*", L. C. Klein, L. F. Francis, M. De. Guire, J. E. Mark, Eds., *Mater. Res. Soc. Symp. Proc.* Warrendale, PA 1999, 546.
[15] J. E. Mark, "*Silicones and Silicone-Modified Materials*", S. J. Clarson, J. J. Fitzgerals, M. J. Owen, S. D. Smith, Eds., *ACS Symp. Ser.* Washington, DC 2000, 1.
[16] J. P. Cohen Addad, L. Dujourdy, *Polym. Bull.* **1998**, *41*, 253.
[17] J.-C. Castaing, C. Allain, P. Auroy, L. Auvray, *Eur. Phys. J. B* **1999**, *10*, 61.
[18] [18a] A. Khalfi, E. Papirer, H. Balard, H. Barthel, M. Heinemann, *J. Colloid Interface Sci.* **1997**, *184*, 586; [18b] E. Nikitina, V. Khavryutchenko, E. Sheka, H. Barthel, J. Weis, *Composite Interfaces* **1999**, *6*, 3; [18c] H. Balard, E. Papirer, A. Khalfi, H. Barthel, *Composite Interfaces* **1999**, *6*, 19.
[19] B. W. Kim, *J. Microelectromechan. Syst.* **2001**, *10*, 33.
[20] C. Martos, F. Rubio, J. Rubio, J. L. Oteo, *J. Sol-Gel Sci. Technol.* **2001**, *20*, 197.
[21] H. Barthel, L. Rosch, J. Weis, in: *Organosilicon Chemistry II: From Molecules to Materials*, N. Auner, J. Weis, Eds., VCH, Weinheim 1996, p. 761.
[22] W. B. Jensen, "The Lewis Acid-Base Concepts: Recent Results and Prospects for the Future", in: *Acid-Base-Interactions*, K. L. Mittal, H. R. Anderson, Eds., VSP, Utrecht 1991, p. 3.
[23] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319.
[24] [24a] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877; [24b] R. W. Taft, M. J. Kamlet, *J. Chem. Soc. Perkin Trans. 2* **1979**, 1723; [24c] M. J. Kamlet, T. H. Hall, J. Bodkin, R. W. Taft, *J. Org. Chem.* **1979**, *44*, 2599.
[25] [25a] S. Spange, E. Vilsmeier, A. Reuter, K. Fischer, S. Prause, Y. Zimmermann, C. Schmidt, *Macromol. Rapid Commun.* **2000**, *21*, 643; [25b] S. Spange, A. Reuter, E. Vilsmeier, D. Keutel, T. Heinze, W. Linert, *J. Polym. Sci.* **1998**, *36*, 1945.
[26] [26a] S. Spange, A. Reuter, E. Vilsmeier, *Colloid Polym. Sci.* **1996**, *274*, 59; [26b] S. Spange, A. Reuter, *Langmuir* **1999**, *15*, 141; [26c] S. Spange, A. Reuter, D. Lubda, *Langmuir* **1999**, *15*, 2103; [26d] S. Spange, Y. Zimmermann, A. Gräser, *Chem. Mater.* **1999**, *11*, 3245.
[27] K. Fischer, S. Prause, S. Spange, F. Cichos, C. von Borczyskowski, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1210.
[28] E. Stathatos, P. Lianos, V. L. Stangar, B. Orel, *Chem. Phys. Lett.* **2001**, *V345*, 381.
[29] F. Cichos, R. Brown, P. A. Bopp, *J. Chem. Phys.* **2001**, *114*, 6834.
[30] A. A. Gorman, M. G. Hutchings, P. D. Wood, *J. Am. Chem. Soc.* **1996**, *118*, 8497.
[31] [31a] S. Spange, C. Schmidt, H. R. Kriecheldorf, *Langmuir* **2001**, *17*, 856; [31b] S. Spange, K. Fischer, S. Prause, T. Heinze, *Cellulose* **2003**, *10*, 201; [31c] K. Fischer, T. Heinze, S. Spange, *Macromol. Chem. Phys.* **2003**, *204*, 1315; [31d] K. Fischer, S. Spange, *Macromol. Chem. Phys.* **2000**, *201*, 1922.
[32] S. Spange, A. Reuter, S. Prause, C. Bellmann, *J. Adhes. Sci. Technol.* **2000**, *14*, 399.
[33] A. A. Schilt, *J. Am. Chem. Soc.* **1960**, *82*, 3000.
[34] S. Spange, D. Keutel, F. Simon, *J. Chim. Phys.* **1992**, *89*, 1615.
[35] S. Spange, E. Vilsmeier, Y. Zimmermann, *J. Phys. Chem. B* **2000**, *104*, 6417.
[36] [36a] Y. Zimmermann, S. Anders, K. Hofmann, S. Spange, *Langmuir* **2002**, *18*, 9578; [36b] Y. Zimmermann, S. Spange, *J. Phys. Chem. B* **2002**, *106*, 12524.
[37] [37a] S. Spange, E. Vilsmeier, *Colloid Polym. Sci.* **1999**, *277*, 687; [37b] S. Prause, S. Spange, *J. Phys. Chem. B* **2004**, *108*, 5734.
[38] F. Besseau, M. Lucon, C. Laurence, M. Berthelot, *J. Chem. Soc. Perkin Trans. 2* **1998**, 101.