

# Adsorption of Polymers on Inorganic Solid Acids Investigated by Means of Coadsorbed Solvatochromic Probes

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The adsorption of five different synthetic polymers, namely, polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), poly(4-vinylpyridine) (PVPy), and poly(*N*-vinylpyrrolidone) (PVP) in a 1,2-dichloroethane or dichloromethane slurry has been studied by measuring the UV/vis spectra of coadsorbed solvatochromic probes. Fe(phen)<sub>2</sub>(CN)<sub>2</sub> [*cis*-dicyano-bis-(1,10)-phenanthroline-iron(II), (**1**)] and Michler's ketone [4,4'-bis(*N,N*-dimethylamino)-benzophenone, (**2**)] were used as solvatochromic surface polarity indicators. The UV/vis transmission spectra of the two surface polarity indicators **1** and **2** adsorbed on silica and alumina, respectively, were measured as a function of the adsorption time of the coadsorbed polymer in slurries in dichloromethane or 1,2-dichloroethane. Kamlet–Taft's  $\alpha$  (hydrogen-bond acidity) parameter of the polymer/solid acid interfaces has been calculated using the linear function of  $\tilde{\nu}_{\max}(\mathbf{1})$  with  $\alpha$  of solid acids after Spange, S.; Vilsmeier, E.; Zimmermann, Y. *J. Phys. Chem. B* **2000**, *104*, 6417. The  $\alpha$  value of alumina significantly decreases on increasing the HBA (hydrogen-bond accepting) capacity of the adsorbed polymer PS < PMMA < PEO < PVPy  $\approx$  PVP. The basic polymer adsorbs preferentially on the Lewis acidic sites of alumina. Adsorption of polymers on silica causes similar effects on  $\tilde{\nu}_{\max}(\mathbf{1})$  as observed for alumina, but the effects cannot be classified in terms of an acid–base interaction model for all polymers, because PVPy and PS show anomalous behavior on adsorption. Determination of  $\pi^*$  (dipolarity/polarizability) parameters of polymer/solid acid interfaces is not possible because of the large  $\pi^*$  value of the solvents used.

## Introduction

Surface functionalization of silica, alumina, and other inorganic oxides with polymers plays an important role in academic research and industrial applications.<sup>1–25</sup> Several efficient procedures for grafting inorganic substrates onto and off polymers have been developed over the past decade.<sup>2,3,5–9</sup>

Physical adsorption of polymers from a solution onto a surface is a very simple procedure and is therefore advantageous<sup>10–25</sup> because time-consuming chemical synthetic steps can be avoided.<sup>10–25</sup> Complete surface functionalization by adsorption occurs if the surface and the polymer are oppositely charged. This can be realized by carrying out polyelectrolyte adsorption from water, for example, polyvinylamine on silica or cellulose.<sup>19–23</sup> However, several commercially available polymers which are of potential interest are insoluble in water. Those polymers include polystyrene (PS) and poly(methyl methacrylate) (PMMA). Other polymers such as poly(ethylene oxide) (PEO), poly(4-vinylpyridine) (PVPy), and poly(*N*-vinylpyrrolidone) (PVP) are soluble in water as well as organic solvents, such as dichloromethane.

Adsorption of uncharged polymers on an inorganic surface in moderately polar organic solvents occurs in different ways depending on the molecular structure, molecular weight, and morphology of the materials.<sup>4,11–14,23,25</sup> The driving force for the adsorption of HBA polymers on silica is the formation of hydrogen bonds between different silanol groups and the lone pairs of electrons on the polymer as evidenced by DRIFT (diffuse-reflectance infrared Fourier transform) spectroscopy and

adsorption calorimetry.<sup>11–13</sup> The alumina as well as the aluminosilicate surface possess both Brønsted and Lewis acidic sites. Polymer adsorption on both solid acids can occur via both sites, dependent on structure of polymer and solvent.<sup>14b,25,27,28</sup> Accordingly, surface acidity of the inorganic solid, basicity of the polymer, and polarity of the solvent are important for understanding the results of the adsorption process. It is not possible to mention all literature cited (see secondary citations in refs 4 and 10–16).

In this paper, we use a specific empirical concept to determine “surface polarity” of inorganic particles, for example, silica, alumina, and aluminosilicate, when uncharged polymers are adsorbed from moderately polar organic solvents.<sup>17–34</sup>

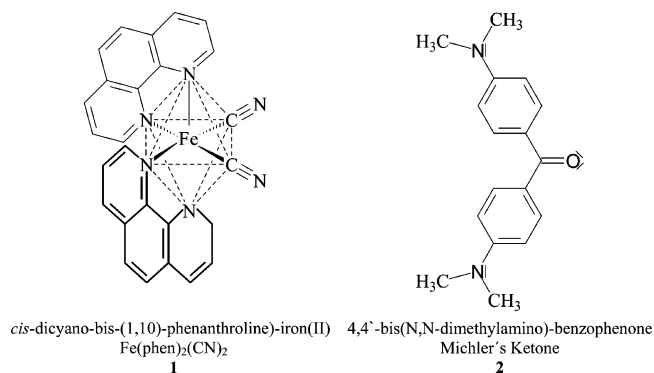
For the determination of surface polarity parameters, the well-accepted Kamlet–Taft linear solvation energy (LSE) relationship and the use of specific solvatochromic and fluorescence UV/vis probes have been established.<sup>29–42</sup> The simplified Kamlet–Taft equation applied to solvatochromic UV/vis shifts ( $XYZ = \tilde{\nu}_{\max, \text{Probe}}$ ) is given in eq 1.<sup>30,31,35,41</sup>

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

$(XYZ)_o$  is the value for the solvents reference system, for example, a nonpolar solvent or the gas phase,  $\alpha$  is the HBD (hydrogen bond donating) ability,  $\beta$  is the HBA (hydrogen bond accepting) ability, and  $\pi^*$  is the dipolarity/polarizability of the solvents.  $\delta$  is a polarizability correction term that is 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents, and zero for aliphatic solvents.  $a$ ,  $b$ ,  $s$ , and  $d$  are solvent-independent regression coefficients.

Jensen<sup>38</sup> recommended the following approach [eq 2] for estimating the adsorption energy of a component, that is, a

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**SCHEME 1: Formulas of the Solvatochromic Probes Used in This Work**


dissolved polymer (p) on an inorganic surface with the help of the Kamlet–Taft parameters.

$$P = P_o + A\alpha_s\beta_p + B\alpha_p\beta_s + C\pi^*_s\pi^*_p \quad (2)$$

$P$ , physicochemical quantity, for example, adsorption enthalpy;

$P_o$ , reference constant relating to a theoretical standard process with  $A = B = C = 0$ ;

$\alpha_s$ , hydrogen bond donating ability of the surface;

$\beta_p$ , hydrogen bond accepting ability of the polymer;

$\alpha_p$ , hydrogen bond donating ability of the polymer;

$\beta_s$ , hydrogen bond accepting ability of the surface;

$\pi^*_p/\pi^*_s$ , dipolarity/polarizability of the polymer and surface, respectively.

The coefficients  $A$ ,  $B$ , and  $C$  are the material's independent regression coefficients which reflect the susceptibility of each of the three different contributions, acid–base ( $A$ ) and reverse ( $B$ ) as well as nonspecific dipolar interactions ( $C$ ) on  $P$ . The larger the product of either  $\alpha_s\beta_p$ ,  $\alpha_p\beta_s$ , or  $\pi^*_s\pi^*_p$ , the more strongly the polymer is likely to be adsorbed on a surface.  $\alpha_s$ ,  $\beta_p$ ,  $\alpha_p$ ,  $\pi^*_s$ , and  $\pi^*_p$  have been reported by us for several polymers and inorganic solid acids.<sup>39,40</sup>  $\text{Fe(phen)}_2(\text{CN})_2$  [cis-dicyano-bis-(1,10)-phenanthroline-iron(II)] (**1**),<sup>43,44</sup> Michler's Ketone [4,4'-bis(*N,N*-dimethylamino)-benzophenone] (**2**),<sup>45</sup> (Scheme 1), and an aminobenzofurandione dye<sup>46</sup> (for  $\beta$  of polymers)<sup>40a,c</sup> have been used as solvatochromic surface polarity indicators for this purpose. Appropriate  $\beta$  values for inorganic solid acids are still not available because of the lack of suitable probes.<sup>47</sup>

In a previous paper, we were able to show that significant UV/vis shifts of **1** and **2**, respectively, take place when adsorbed on silica by coadsorption of PEO in 1,2-dichloroethane.<sup>48</sup> In particular, the HBD capacity of the silica surface decreases with PEO adsorption.

The goal for this specific research was to determine how the surface acidity ( $\alpha_s$ ) and polymer basicity ( $\beta_p$ ) affect the resulting  $\alpha$  and  $\pi^*$  parameter of the composite.

It is expected that the larger the product of  $\alpha_s\beta_p$ ,  $\alpha_p\beta_s$ , and  $\pi^*_s\pi^*_p$ , respectively, the stronger will be the adsorption to be measured by coadsorption of a solvatochromic probe. This consideration determined the choice of inorganic solid acids and polymers for an extended study. For this study, three inorganic solid acids, silica ( $\alpha_s = 1.06$ ), alumina ( $\alpha_s = 1.46$ ), and aluminosilicate (Siral 40) ( $\alpha_s = 1.84$ ), have been chosen.<sup>49</sup> Accordingly, certain polymers have been used which significantly differ in their basicity: polystyrene (PS) ( $\beta_p = 0.28$ ,  $\pi^*_p = 0.66$ ), poly(methyl methacrylate) (PMMA) ( $\beta_p = 0.38$ ,  $\pi^*_p = 0.71$ ), poly(ethylene oxide) (PEO) ( $\beta_p = 0.65$ ,  $\pi^*_p = 0.86$ ), poly(4-vinylpyridine) (PVPy) ( $\beta_p = 0.83$ ,  $\pi^*_p = 0.85$ ), and poly(*N*-vinylpyrrolidone) (PVP) ( $\beta_p = 0.93$ ,  $\pi^*_p = 0.93$ ).<sup>36,40a</sup> The

**TABLE 1: Physical Properties, Chemical Characteristics, and Source of the Polymers Used in This Work**

polymer	$M_w$ (g mol <sup>-1</sup> )	acidity $\alpha$	basicity $\beta$	dipolarity/ polarizability $\pi^*$	producer/ source
PS	45 000	0	0.28	0.66	Acros
PMMA	120 000	0	0.38	0.71	Acros
PEO	100 000	0	0.65	0.86	Acros
PVPy	176 000	0.06	0.83	0.85	Merck
PVP	25 000	0.01	0.93	0.93	Polysciences

$\alpha$  values of these polymers can be neglected.<sup>40a</sup> The dipolarity/polarizability is similar for all samples. Physical properties and chemical characteristics of the inorganic solid acids and polymers are given in the Experimental Section.

**Experimental Section**

**Materials.** Physical properties, chemical characteristics, and source of the polymers and solid acids used in this work are given in Tables 1 and 2.

1,2-Dichloroethane and dichloromethane were dried ( $\text{CaH}_2$ ), freshly distilled before use, and stored over basic  $\text{Al}_2\text{O}_3$ .  $\text{Fe(phen)}_2(\text{CN})_2$  was prepared according to Schilt.<sup>50</sup> Michler's ketone was purchased from Merck, recrystallized twice from ethanol, and dried over  $\text{CaH}_2$  before use. Spectroscopic grade 2,6-di-*tert*-butylpyridine (DTBP) was purchased from Merck.

**UV/Vis Measurements.** The equipment employed was a UV/vis spectrometer MCS 400 connected to an immersion cuvette TS 5A (Zeiss). 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.<sup>49</sup>

The solids were heated at 400 °C for 8 h. After cooling to room temperature under dry argon, a measured quantity was introduced into the measurement cell and immediately suspended in the solvent. Then, a solution of the probe dye in the same solvent was added to this slurry. The reproducibility of the UV/vis spectra of the adsorbed dyes is very good with  $\Delta\lambda_{\text{max}} < 1$  nm.

Careful sample preparation is necessary to achieve correct reproduction of the quality of the UV/vis spectrum of the adsorbed dyes on alumina. Alumina must always be freshly prepared. Storage for 24 h after the thermal pretreatment results in readsorption of water traces despite inert conditions (argon atmosphere). 1,2-Dichloroethane and dichloromethane have been used as the standard solvent, because all polymers used as well as the solvatochromic probes are readily soluble in them. Furthermore, the inorganic solids form transparent slurries in these solvents which allows one to take good quality transmission UV/vis spectra.

The polymer is dissolved either in 1,2-dichloroethane (PS, PMMA, PEO) or dichloromethane (PVPy, PVP) and a stock solution is used for the adsorption experiments. The quantity of adsorbed polymer was determined by quantitative elemental analysis of the polymer/solid acid composites. For this purpose, the composite was filtered off, dried carefully, and analyzed.

**Determination of the Polarity Parameters.** For the determination of the surface acidity  $\alpha$ , a re-correlated LSE relationship [eq 3] was used, derived from the  $\tilde{\nu}_{\text{max}}$  (**1**) values when adsorbed on various solid acids and the calculated parameters  $\alpha$ . Data are taken from our previous paper.<sup>49</sup>

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

$$n = 33, r = 0.99, \text{sd} = 0.03 \quad (3)$$

**TABLE 2: Physical Properties, Chemical Characteristics, and Source of the Solid Acids Used in This Work**

solid acid	BET-surface area (m <sup>2</sup> g <sup>-1</sup> )	mean pore diameter (nm)	acidity $\alpha$	dipolarity/polarizability $\pi^*$	producer
Aerosil 300	240	<sup>a</sup>	1.06	0.85	Degussa
Al <sub>2</sub> O <sub>3</sub>	100	11.4	1.46	0.37	Degussa
Siral 40	460	3.5	1.84	0.43	Condea

<sup>a</sup> For measured, but not detectable.

This equation is statistically significant and allows the determination of  $\alpha$  values in relation to our previous work without the knowledge of  $\tilde{\nu}_{\max}$  data of a second UV/vis probe like **2**.

**BET (Brunau Emmett Teller) Measurements.** The BET surface area was measured with nitrogen at 77 K using a Sorptomatik 1900 (Fisons).

**Correlation Analyses.** The correlation analyses were carried out using statistic tool of Microcal Origin version 5.0 SR2 from Microcal Software.

## Results and Discussion

**Preliminary Studies.** The dye is adsorbed onto the surface of the solid from its solution very well as long as the polarity or HBD strength difference between the solvent and the surface of the solid is large enough. The probes used for this study are moderately strong bases which correspond to basicity values of about  $\beta_1 = 0.5 \pm 0.2$  ( $\beta_1$  denotes the basicity of the solvatochromic indicator as a solute).<sup>30,51</sup> For **2**, a  $\beta_1$  value of 0.67 was reported on the basis of infrared spectroscopic results.<sup>51</sup>

The probes used are mobile and they detect the strongest polar site on the surface with respect to its own structure, corresponding to a minimum of free energy of adsorption. It is proposed that there are three possible types of sites in these inorganic solid acid/probe/polymer system: (a) probe partitioned within the polymer, which is adsorbed to the inorganic acid surface, (b) probe located at the interface between the polymer and the solid acid, and (c) solvated probe located at the polymer/solid acid interface.<sup>38,39</sup> This problem is illustrated in Scheme 2 and the possible localization sites (a, b, c) of the probe (P) are indicated.

Accordingly, three different experimental observations are expected dependent on the associated behavior of the polymer and probe when coadsorbed on the inorganic surface.

**Option (OI).** The polymer adsorbs completely on the surface and the dye desorbs. A large  $\alpha_s\beta_p$  value is expected, that is,  $\alpha_s\beta_p \gg \alpha_s\beta_1$ . In this case, the UV/vis spectrum shows contributions of the adsorbed and dissolved dye fraction.

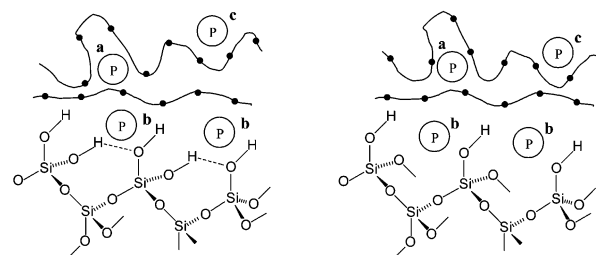
**Option (OII).** The polymer coadsorbs beside the probe dye but hardly affects the original adsorption site of the dye. A low  $\alpha_s\beta_p$  value is expected, that is,  $\alpha_s\beta_p \ll \alpha_s\beta_1$ . The UV/vis spectrum remains the same, before and after the adsorption of the dye.

**Option (OIII).** The polymer coadsorbs on the surface beside the probe dye. For this case, moderate  $\alpha_s\beta_p$  values are expected, that is,  $\alpha_s\beta_p \geq \alpha_s\beta_1$ . A spectral shift is observed, because the dye is displaced by the polymer, either because a site within the polymer is more favorable for adsorption of the dye or the polymer is a stronger HBA than the dye.

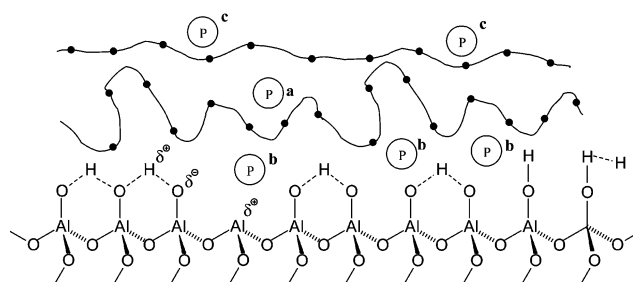
The strong solid acid aluminosilicate interacts strongly with the basic polymers and proton transfer from the surface takes place upon the probe mediated by the adsorbed polymer. As a consequence of this reaction, the UV/vis spectra of the probes in the presence of aluminosilicate show the protonated form of **1**<sup>50</sup> and **2**.<sup>49b</sup> A similar result was obtained when **1** and **2**, respectively, are adsorbed on HY zeolite or aluminosilicate from acetonitrile, nitromethane, or acetone.<sup>54,55</sup> Proton migration on

**SCHEME 2: Possible Locations of a Solvatochromic Probe at the Polymer/Solid Acid Interface in a Solvent<sup>a</sup>**

2.1



2.2



<sup>a</sup> 2.1: on silica (left: geminal silanol groups; right: isolated silanol groups); 2.2: on alumina. The typical sites a, b, and c are indicated, respectively.

the probe mediated by the solvent took place which caused unreasonably large  $\alpha$  values.<sup>55</sup> For that reason, aluminosilicate was abandoned for those studies and we used a silica (Aerosil 300,  $\alpha = 1.06$ ,  $\pi^* = 1.0$ ) and an alumina ( $\alpha = 1.45$ ,  $\pi^* = 0.70$ ) batch for this work.

The extent of the solvatochromic shift is also dependent on the concentration of adsorbed polymer and the adsorption time. Typical Langmuir adsorption isotherms are obtained.<sup>47,48</sup> About 60 mg polymer per 300 mg solid acid is necessary to achieve complete surface coverage in 1,2-dichloroethane or dichloromethane. For the evaluation, we used the greatest solvatochromic shift  $\Delta\lambda$  observed as function of concentration of polymer. Qualitative results concerning the solvatochromic effects observed in relation to  $\alpha_s\beta_p$  values are compiled in Table 3.

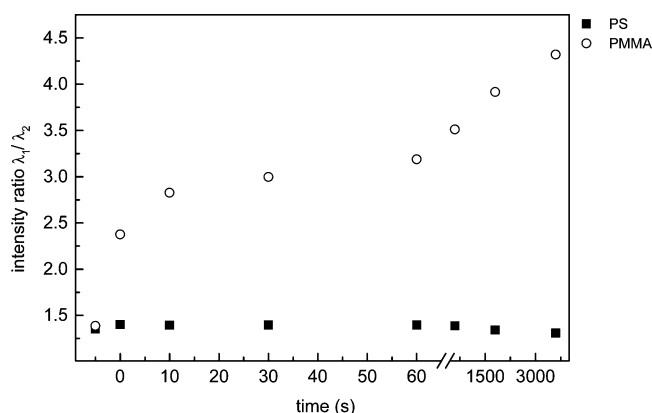
The results in Table 3 show that acid–base interactions between the polymer and the inorganic surface can be measured using dye **1**, whereas the dipolar/dipolar interaction is not detectable by a solvatochromic shift. The latter effect cannot be observed using the two solvatochromic probes. This is not surprising because the dipolarity/polarizability of 1,2-dichloroethane ( $\pi^* = 0.81$ ) or dichloromethane ( $\pi^* = 0.82$ ) are in the same order of magnitude as those of the polymers, but the basicity of these solvents are minimal ( $\beta \leq 0.1$ ).

Low  $\alpha_s\beta_p$  values correspond to weak solvatochromic effects. Because the probes possess  $\beta_1$  values in the range of  $\sim 0.6$ ,

**TABLE 3: Qualitative Solvatochromic Effects of Coadsorbed Probes 1 and 2, Respectively, Observed for Polymer/Solid Acid Compositions Studied in This Work in Relation to  $\alpha_s \beta_p$  Values and the Expected Effect OI, OII, and OIII on the UV/Vis Spectra**

polymer/solid acid	$\alpha_s \beta_p$	impact on solvatochromism	
		1	2
PS/Aerosil 300	0.30	unprecedented weak effect <sup>a</sup>	no measurable effect
PMMA/Aerosil 300	0.40	weak effect according to OIII, $\Delta\lambda_{\max,1} = 2$ nm	desorption of probe according to OI
PEO/Aerosil 300	0.69	expected effect according to OIII, $\Delta\lambda_{\max,1} = 14$ nm	desorption of probe according to OI
PVPy/Aerosil 300	0.88	reversible adsorption <sup>b</sup>	desorption of probe according to OI
PVP/Aerosil 300	0.98	expected effect according to OIII, $\Delta\lambda_{\max,1} = 8$ nm	desorption of probe according to OI
PS/alumina	0.41	no measurable effect	no measurable effect
PMMA/alumina	0.55	expected effect according to OIII, $\Delta\lambda_{\max,1} = 6$ nm	desorption of probe according to OI
PEO/alumina	0.95	expected effect according to OIII, $\Delta\lambda_{\max,1} = 16$ nm	desorption of probe according to OI
PVPy/alumina	1.21	expected effect according to OIII, $\Delta\lambda_{\max,1} = 22$ nm	desorption of probe according to OI
PVP/alumina	1.36	expected effect according to OIII, $\Delta\lambda_{\max,1} = 21$ nm	desorption of probe according to OI

<sup>a</sup> Hypsochromic effect, see text. <sup>b</sup> Oscillating adsorption, see text.



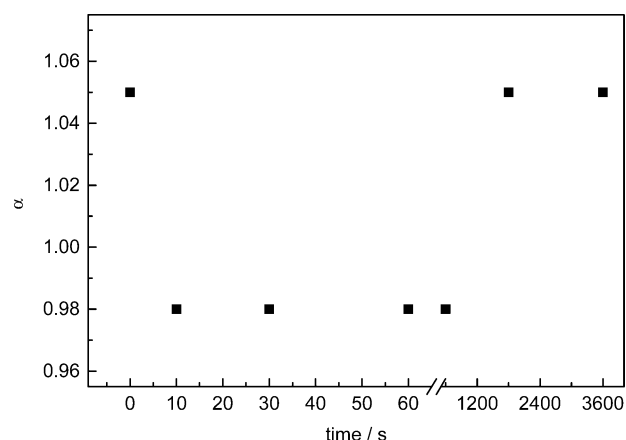
**Figure 1.** Intensity ratio of the two UV/vis absorption maxima of **2** on the surface ( $\lambda_2 = 387$  nm) and in the supernatant solution ( $\lambda_1 = 350$  nm) as a function of time when measured in a slurry of 300 mg silica when 60 mg PS and PMMA, respectively, have been coadsorbed,  $T = 293$  K.

polymers with low  $\beta_p$  values do not have any influence on the solvatochromic shift of the adsorbed probe. In the following, we present the solvatochromic results of polymer/solid compositions in detail.

**Adsorption on Silica.** Coadsorbed polystyrene on silica does not cause a bathochromic solvatochromic shift of the adsorbed probe **1**. A hypsochromic shift of **1** ( $\Delta\lambda = -6$  nm) is observed when 100 mg PS is coadsorbed on 300 mg Aerosil 300. The UV/vis shift is time dependent:  $\lambda_{\max}(\mathbf{1}) = 539$  nm before PS is added;  $\lambda_{\max}(\mathbf{1}) = 536$  nm after 30 min; and  $\lambda_{\max}(\mathbf{1}) = 533$  nm after 20 h adsorption time. This effect is not caused by acidic impurities or HCl traces from the solvent. It indicates an apparent increase of the HBD capacity and may be explained by the theory that PS occupies hydrophobic sites on the silica surface and thus **1** then measures an average of more acidic sites than before adsorption of the polymer.<sup>53</sup>

PMMA adsorbs readily and causes a small bathochromic effect on coadsorbed **1** because the strongest acidic sites are occupied by the HBA polymer. **2** desorbs from silica as the adsorption time of PMMA increases, indicated by the appearance of the characteristic UV/vis absorption of **2** in 1,2-dichloroethane at  $\lambda_{\max}(\mathbf{2}) = 350$  nm (Figure 1).

PVPy is a strong basic polymer which finds many applications in materials science and surface functionalization. Immediately after adsorption of PVPy on silica, a significant bathochromic shift of adsorbed **1** from  $\lambda_{\max}(\mathbf{1}) = 536$  nm ( $\alpha = 1.05$ ) to  $\lambda_{\max}(\mathbf{1}) = 541$  nm ( $\alpha = 0.98$ ) is observed. Then, in the mixture readorption of **1** takes place and, therefore, a UV/vis band of **1** is observed which is similar to that before PVPy was added (see Figure 2).



**Figure 2.** Alteration of the surface acidity of the silica/PVPy interface as a function of time as measured by coadsorbed **1** in dichloromethane at 293 K.

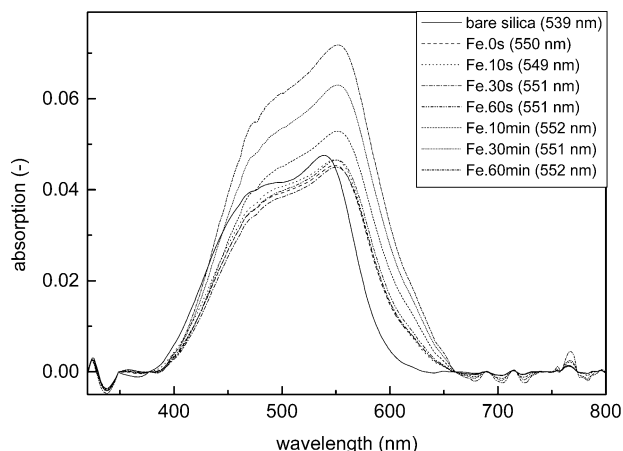
We explain this effect in terms of the oscillating adsorption of PVPy on silica, which is a well-established phenomenon.<sup>56</sup> However, the oscillating adsorption of PVPy on silica provides permanently accessible acidic sites which can be occupied by the solvatochromic probes. Using **2** as the probe, a fraction of the dye partly desorbs. A UV/vis shift of the coadsorbed probe fraction of **2** is not observed when PVPy is coadsorbed. However, despite the interference caused by redesorption of PVPy from silica, the solvatochromic method is suitable for detecting this specific effect.

Adsorption of PEO on silica has been studied by several authors<sup>12,23</sup> because of its strong adsorption which can be measured readily by different techniques.

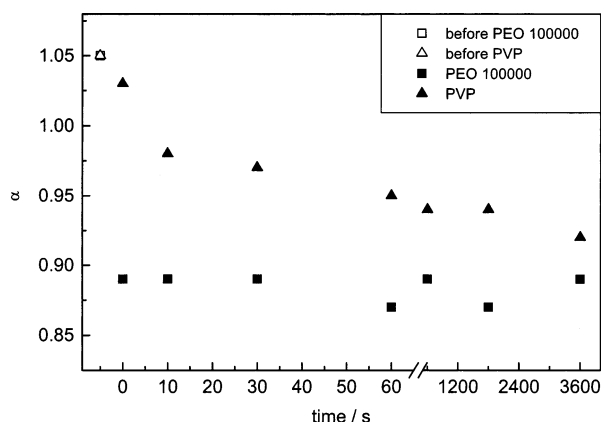
As an extension to our previous study,<sup>48</sup> we investigated the influence of the molecular weight on the solvatochromic shift of coadsorbed **1**. Figure 3 shows a typical UV/vis spectra series of **1** when PEO ( $M_w = 10\,000$  g mol<sup>-1</sup>) is coadsorbed on silica as function of adsorption time.

A significant bathochromic shift of **1**-loaded silica when PEO ( $M_w = 10\,000$  g mol<sup>-1</sup>) is coadsorbed takes place from  $\lambda_{\max}(\mathbf{1}) = 539$  nm to about  $\lambda_{\max}(\mathbf{1}) = 550$  nm corresponding to a decrease of the HBD capacity of the silica/PEO interface from  $\alpha = 1.06$  to  $\alpha = 0.87$  after 1 h. Oligomers of PEO ( $M_w = 1000$  g mol<sup>-1</sup>) adsorb slightly more strongly and  $\alpha$  decreases up to 0.85. Reorganization of adsorbed PEO chains ( $M_w = 10\,000$  g mol<sup>-1</sup>) finally results in a moderate HBD capacity of the silica/PEO interface of  $\alpha = 0.85$  after 6 h adsorption time. The time-dependent measured UV/vis shift of **1** shown by the corresponding  $\alpha$  values is shown in Figure 4. Using high molecular weight PEO ( $M_w = 100\,000$  g mol<sup>-1</sup>), a smaller





**Figure 3.** UV/vis spectra of **1**-loaded silica after adsorption of PEO ( $M_w = 10\,000\text{ g mol}^{-1}$ ) as a function of adsorption time in 1,2-dichloroethane.

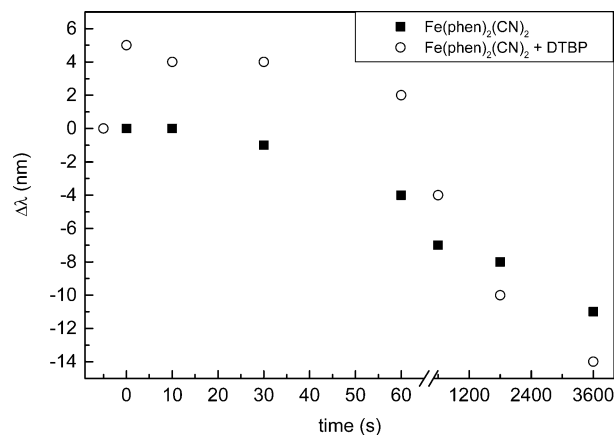


**Figure 4.**  $\alpha$  of the PEO/silica and PVP/silica interface as a function of adsorption time.

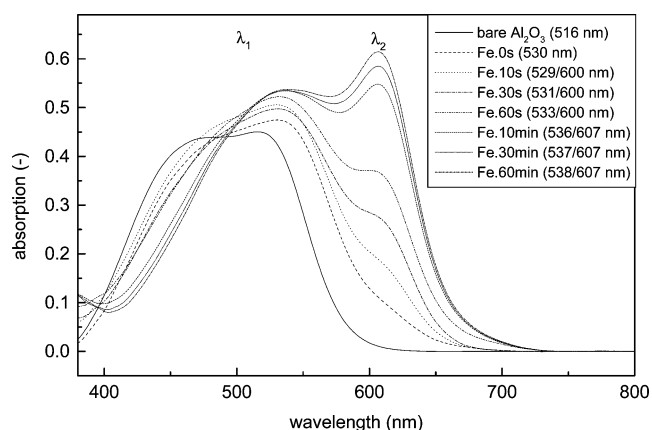
decrease in the surface acidity is observed to  $\alpha = 0.9$  (see Figure 4) independent of the adsorption time period.

Despite the evidently larger HBA capacity of PVP compared to PEO, adsorption of PVP on silica causes a weaker bathochromic shift of **1** when adsorbed on silica. Perhaps, dissolved PVP contains water impurities which are responsible for this effect, because water shows a large polarity.<sup>31–34</sup> The time-dependent measured UV/vis shift of **1** expressed in terms of the corresponding  $\alpha$  values is shown in Figure 4.

**Adsorption on Alumina.** Probe **1** readily adsorbs on alumina. The typical UV/vis absorption band with a clear maximum at  $\lambda_{\max}(\mathbf{1}) = 516\text{ nm}$  ( $\alpha = 1.45$ ) always results on alumina after 1 h adsorption time. The UV/vis band of the adsorbed **1** has been utilized as described in our previous paper.<sup>49a</sup> The UV/vis absorption maximum of  $\text{Fe(phen)}_2(\text{CN})_2$  on alumina when immediately adsorbed from 1,2-dichloroethane appears at  $\lambda_{\max}(\mathbf{1}) = 525\text{ nm}$  indicating acidic sites with  $\alpha = 1.26$ . After 30 s, the UV/vis band of adsorbed  $\text{Fe(phen)}_2(\text{CN})_2$  undergoes a hypsochromic shift which remains constant at  $\lambda_{\max}(\mathbf{1}) = 510\text{--}516\text{ nm}$  after 1 h adsorption time. It is possible that migration of  $\text{Fe(phen)}_2(\text{CN})_2$  from weaker Brønsted to stronger Lewis acidic sites occurs. To decide at which surface site **1** is adsorbed, a competition experiment using 2,6-di-*tert*-butylpyridine was carried out. The strong Brønsted base 2,6-di-*tert*-butylpyridine can interact with mobile protons on a surface<sup>57</sup> but not with Lewis acid sites,<sup>55</sup> because the two sterically demanding *tert*-butyl groups in the 2- and 6-positions of the pyridine ring prevent the attack of a Lewis acid on the lone electron pair of the nitrogen atom.



**Figure 5.** Shift of the UV/vis absorption maximum of **1** as a function of time when adsorbed on 300 mg alumina immediately after adsorption from 1,2-dichloroethane (■) and after the addition of a 50-fold excess of 2,6-di-*tert*-butylpyridine with respect to **1** (○).

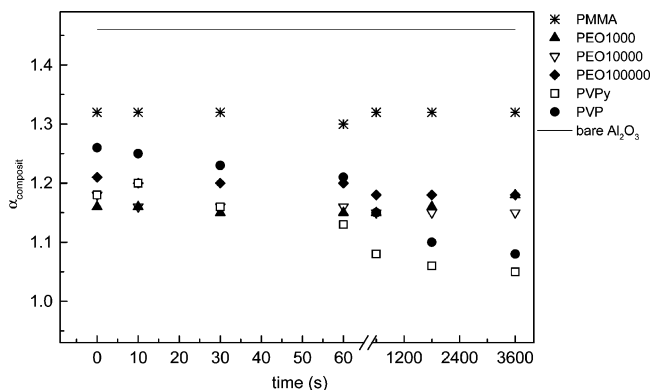


**Figure 6.** Time-dependent UV/vis spectra series monitored of **1**-loaded alumina when 60 mg PVPy has been adsorbed in dichloromethane.

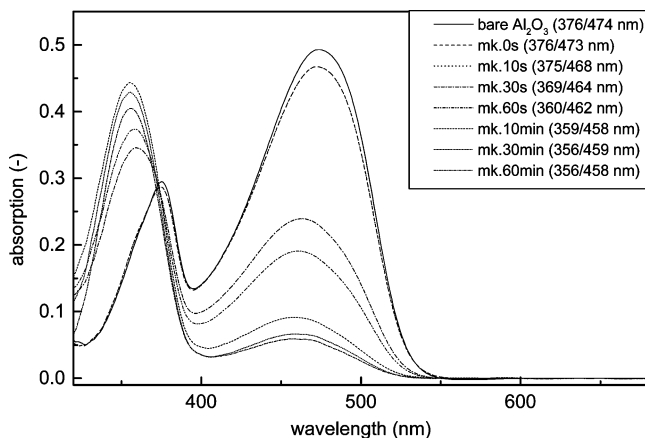
Since 2,6-di-*tert*-butylpyridine is added [50-fold excess with respect to  $\text{Fe(phen)}_2(\text{CN})_2$ ] immediately after complete adsorption of **1** on alumina, a bathochromic shift ( $\Delta\lambda = 5\text{ nm}$ ) of the UV/vis absorption of  $\text{Fe(phen)}_2(\text{CN})_2$  is observed. The UV/vis shift indicates a decrease in the surface Brønsted acidity of alumina, because 2,6-di-*tert*-butylpyridine ligates the fraction of highly acidic mobile protons on the surface. Then after 60 s, a dramatic hypsochromic shift takes place to  $\lambda_{\max}(\mathbf{1}) = 510\text{ nm}$  indicating the migration of  $\text{Fe(phen)}_2(\text{CN})_2$  to stronger acidic Lewis sites. The stronger hypsochromic shift observed in the presence of 2,6-di-*tert*-butylpyridine is a clear indication that weaker acidic sites derived from Brønsted centers are bonded by the sterically hindered base while the stronger Lewis acidic sites remain unaffected by it. We think that the accessibility of the Lewis acid sites in pores is restricted by their geometry and thus slows kinetics in the competition for acid sites on the surface of the polymer, and the dye must also be considered.

PS adsorption does not induce a UV/vis shift of **1**-loaded alumina. However, strongly basic polymers such as PVP or PVPy compete with the adsorbed probe **1**. Thus, **1** desorbs from the alumina surface when excess PVPy has been added (option **OI**). The desorption process of **1** induced by added PVP or PVPy requires a time period of 1 h. The corresponding UV/vis spectra series of dye **1** is shown in Figure 6.

Immediately after addition of PVPy, a bathochromic shift of  $\Delta\lambda = 15\text{ nm}$  of the adsorbed probe fraction of **1** is observed indicating a decrease in the surface acidity. Then, after 10 s, the desorption of **1** from the surface takes place associated with



**Figure 7.**  $\alpha$  as a function of adsorption time when 60 mg PMMA, PEO, PVP, and PVPy, respectively, have been adsorbed on 300 mg alumina in 1,2-dichloroethane or dichloromethane at room temperature.



**Figure 8.** Time-dependent UV/vis spectra series monitored during the adsorption of 60 mg PMMA on 300 mg 2-loaded alumina in 1,2-dichloroethane slurry.

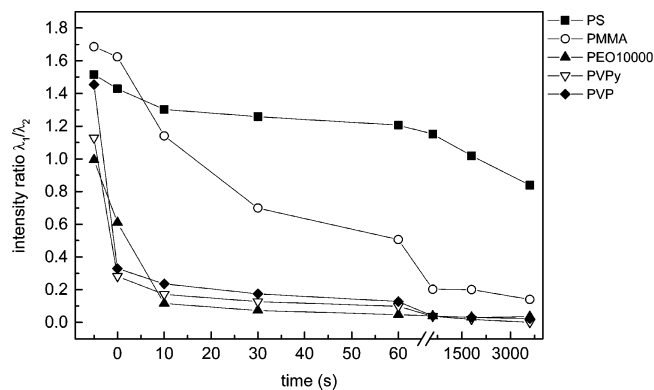
the appearance of the UV/vis spectrum of the dissolved probe at  $\lambda_{\max}(\mathbf{1}) = 607$  nm in the supernatant solvent, which changes from colorless to blue. The reversibility of adsorption of **1** caused by the polymer competition requires a time period similar to that for the migration of **1** to the Lewis acid sites. This result is a clear indication that no chemical reaction of **1** with the solvent or surface takes place.

The UV/vis spectra of the remaining fraction of **1** adsorbed on alumina have been plotted as functions of adsorption time for the HBA polymers. The plots are shown in Figure 7.

Altogether, adsorption of HBA polymers on alumina causes a significant decrease in the surface acidity from  $\alpha = 1.45$  to 0.95 depending on the HBA capacity of the polymer (see Summary).

Adsorption of basic polymers on 2-loaded alumina causes a strong decrease in the UV/vis absorption band intensity at  $\lambda_1 = 470$  nm. This UV/vis band indicates that dye **2** is adsorbed on Lewis acid sites.<sup>49,57</sup> The intensity of the UV/vis absorption of **2** in the supernatant solution (dissolved dye fraction) at  $\lambda_2 = 360\text{--}370$  nm increases with increasing adsorption time. Thus, the intensity ratio of the two UV/vis bands at  $\lambda_1 = 470$  to  $\lambda_2 = 360/370$  is a measure of dye desorption. A typical UV/vis spectra series demonstrating this measurement for PMMA adsorption on alumina is shown in Figure 8.

The intensity ratio of the two UV/vis bands of 2-loaded alumina  $\lambda_1/\lambda_2$  in the slurry decreases with increasing adsorption time, because some of **2** desorbs in the solution phase. The effect



**Figure 9.** Intensity ratio of the two UV/vis bands  $\lambda_1/\lambda_2$  of 2-loaded alumina as a function of time during adsorption of various polymers in 1,2-dichloroethane or dichloromethane slurry.

is more pronounced the larger the  $\beta$  value of the adsorbed polymer is. The curves are shown in Figure 9.

This is a clear indication that adsorption of basic polymers occurs preferentially at Lewis acidic sites on the alumina surface, because the second UV/vis band of **2** on alumina at  $\lambda_{\max}(\mathbf{2}) = 380$  nm remains unaffected. This UV/vis band is attributed to Brønsted acidic sites.<sup>49,57</sup>

Even PS adsorption induces a weak decrease in the intensity of the UV/vis band of **2** at  $\lambda_1 = 470$  nm. However, this does not disappear, indicating that PS does not compete strongly with adsorbed **2**. The time-dependent change in the intensity ratio of the two UV/vis bands provides a qualitative indication of the time scale of adsorption of basic polymers on Lewis acid sites on alumina.

## Summary

1- and 2-loaded silica and alumina samples have been used as adsorbents for various polymers. With increasing basicity of the polymer, increased competition with the preadsorbed probe **1** or **2** takes place. This is indicated by desorption of the probe in the solvent phase or characteristic changes in the UV/vis spectrum of both the adsorbed probe dye fraction and supernatant solution. 1-loaded samples show a significant bathochromic shift of the UV/vis absorption band which corresponds clearly to a decrease in the surface acidity. In other words, the probe migrates to lower acidic sites on the surface because the polymer occupies the strongest acidic sites. The less basic polymer PS shows a negligible effect, because the basicity of the solvatochromic probe is evidently larger than that of the polymer.

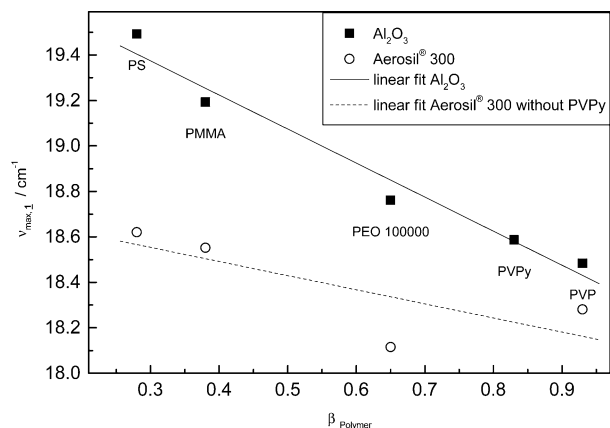
Figure 10 shows both  $\alpha$  of the polymer/silica and polymer/alumina composites as a function of the respective HBA capacities of the polymer component. The polymer loading was 60 mg per 300 mg solid acid. The PVPy/silica system was not considered in this diagram because of the anomalous behavior observed.

As the HBA capacity of the polymer is increased, the acidity of the resulting polymer/solid acid composite decreases. For silica/polymer composites, a trend is only observed because PEO shows a larger effect than nitrogen-containing polymers such as PVP or PVPy (eq 4).

$$\tilde{\nu}_{\max}(\mathbf{1})_{\text{Aerosil300}} 10^{-3} [\text{cm}^{-1}] = 18.74 - 0.62 \beta_{\text{polymer}} \quad (4)$$

$n = 5, r = 0.77, \text{sd} = 0.18$

The result as a whole is in agreement with the influence of HBA solvents on the UV/vis absorption of 1-loaded Aerosil 300



**Figure 10.** HBD capacity of polymer/silica and polymer/alumina composites as a function of  $\beta$ , the HBA capacity, of the polymer component.

samples. Equation 5a and 5b was taken from a recent reference.<sup>58</sup>

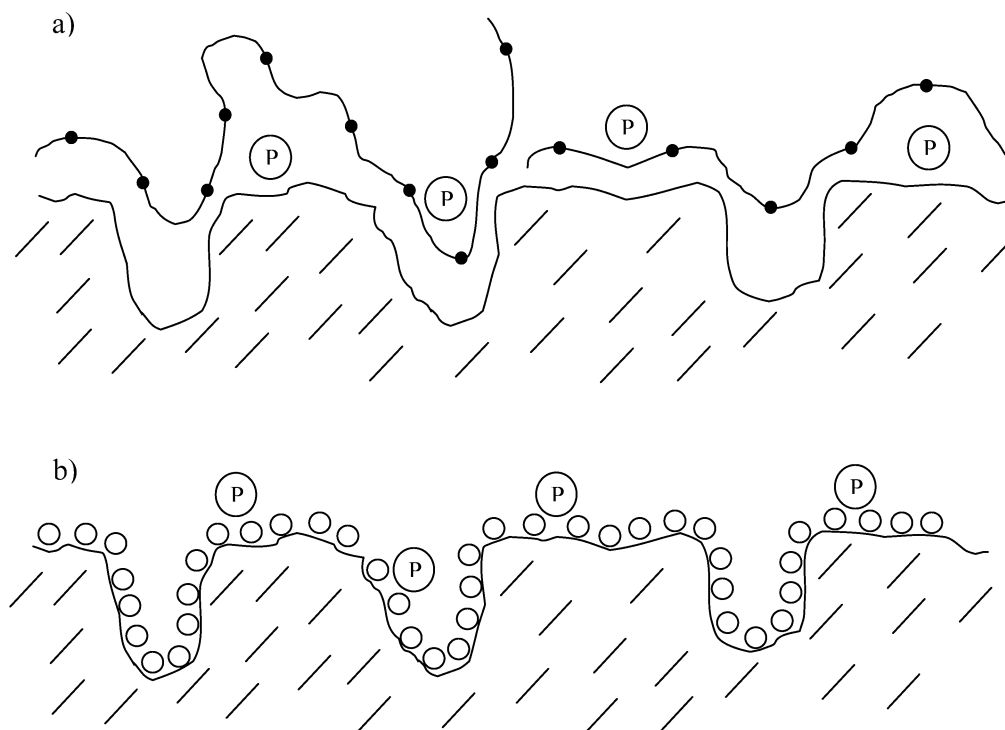
$$\tilde{\nu}_{\max}(\mathbf{1})_{\text{Aerosil300}} 10^{-3} [\text{cm}^{-1}] = 19.02 - 1.65 \beta_{\text{solvent}} \quad n = 13, r = 0.58, \text{sd} = 0.46 \quad (5a)$$

Several solvents, like nitromethane, acetonitrile, or anisole, show anomalous behavior. If they are excluded from the correlation, an improved LSE relationship results.

$$\tilde{\nu}_{\max}(\mathbf{1})_{\text{Aerosil300}} 10^{-3} [\text{cm}^{-1}] = 18.99 - 3.31 \beta_{\text{solvent}} \quad n = 8, r = 0.94, \text{sd} = 0.19 \quad (5b)$$

This result for the influence of solvent relates to that obtained for HBA polymers on silica. However, the influence of solvent upon the HBD capacity of silica is more pronounced than that of adsorbed polymer as indicated by the slope  $\Delta \tilde{\nu}_{\max}(\mathbf{1})/\Delta \beta$ .

**SCHEME 3:** Suggested Options of the Location of Solvatochromic Probes on (a) HBA Polymer/Solid Acid Composite in Weak HBA Solvent ( $\beta = 0.1$ ) and (b) HBA Solvent ( $\beta > 0.4$ )/Solid Acid Particles Slurry



We explain this result in terms of the higher mobility of HBA solvent molecules which cover the HBD surface more effectively.

The slope  $\Delta \tilde{\nu}_{\max}(\mathbf{1})/\Delta \beta$  for polymer/alumina composites (eq 6) is evidently larger than for polymer/silica composites indicating the stronger influence of acid–base interaction between the alumina surface and the adsorbed polymer.

$$\tilde{\nu}_{\max}(\mathbf{1})_{\text{Alumina}} 10^{-3} [\text{cm}^{-1}] = 19.82 - 1.50 \beta_{\text{polymer}} \quad n = 5, r = 0.98, \text{sd} = 0.09 \quad (6)$$

For the influence of solvent on the UV/vis absorption of **1**-loaded alumina, a related correlation has been found (eq 7).<sup>55</sup>

$$\tilde{\nu}_{\max}(\mathbf{1})_{\text{Alumina}} 10^{-3} [\text{cm}^{-1}] = 20.41 - 2.66 \beta_{\text{solvent}} \quad n = 7, r = 0.97, \text{sd} = 0.11 (\beta_{\text{solvent}} > 0.3) \quad (7)$$

However, eq 7 has been calculated for another alumina batch, but with the same potential Lewis acidity strength ( $\alpha \approx 1.4$ ),<sup>55</sup> indicating that the interpretation of our results is valid. It shows that HBA solvents strongly interact with alumina surfaces because they access the Lewis acidic sites in pores better.

For instance, PMMA adsorption on alumina and effective surface coverage is also significantly dependent on the tacticity of the polymer,<sup>25</sup> which shows that steric effects play an important role. Isotactic PMMA covers the surface of alumina more effectively than atactic PMMA.<sup>25</sup>

The difference between HBA solvent and HBA polymer adsorption on a solid acid surface and the influence upon a coadsorbed solvatochromic probe is discussed in Scheme 3.

We think that the solvatochromic probes are reversibly adsorbed on moderately acidic sites on the surface of the solid together with the polymer. As the polymer can exist in various conformations, such as the tail, loop, or train, it can reversibly occupy other sites so that the probe can always occupy the most

acidic of the free sites on the surface. Therefore, solvatochromic probes always measure a larger average acidity when HBA polymers are adsorbed on covered inorganic particles, compared to adsorbed solvents of related HBA strength. The latter cover the acidic surface more effectively.

## Conclusion

The competitive interaction of solvatochromic probe compared with a polymer with a surface environment of silica and alumina can be investigated by measuring the shift of the UV/vis absorption band of a coadsorbed solvatochromic probe such as Fe(phen)<sub>2</sub>(CN)<sub>2</sub> and Michler's ketone in transparent slurries. Thus, the solvatochromic probe is used as a polymer/solid acid interfacial polarity indicator. Acid–base interactions dominate between the polymer and the external solid acid surface of alumina as shown by the correlation analyses of  $\tilde{\nu}_{\max}$  (1) with the Kamlet–Taft polarity parameters of the polymer. Dipole–dipole interactions and weak acid–base interaction changes on polymer adsorption cannot be observed by the probes employed.

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