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Polarities of Sol−Gel-Derived Ormosils and of Their Interfaces with Solvents

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The effective polarities of a series of organically modified sol−gel silicas and of their interfaces were probed using the solvatochromic dye $E_T(30)$ (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate). The series of materials was obtained by copolymerizing, in various proportions, of methyltrimethoxy-, vinyltrimethoxy-, propyltrimethoxy-, isobutyltrimethoxy- and phenyltrimethoxysilanes with tetramethoxysilane. The various doped Ormosils are solvatochromic toward organic solvents such as various alcohols and toluene. Trends in the polarity variation as a function of the monomer type, of its proportion, and of the solvent at the interface were identified and are discussed. These materials can be used as solvent sensors.

Introduction

Organically doped/organically modified sol−gel materials (Ormosils, in the case of silica-based materials)[1,2] have emerged in recent years as successful products.[3] Organic modification of ceramic sol−gel materials is a convenient way of controlling the material properties through the rich library of metal alkoxide monomers bearing a nonhydrolizable substituent.[1−4] Indeed, the literature describing this route is voluminous and is based on a variety of synthetic strategies.[5] Here we greatly extend our preliminary report[6] on the polarity properties of a series of methyltrimethoxysilane/tetramethoxysilane (MeTS/TMOS) Ormosils and on the effective interfacial polarities of these materials when exposed to various solvents (which were used for their sensing as well). The entrapped solvatochromic dye $E_T(30)$ (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)-phenolate (Reichardt's dye)[7] was used for that purpose, and correlation with morphological features, determined by small-angle X-ray scattering (SAXS) experiments, was identified.[6] We explore here the scope of the phenomena we reported in ref 6, by extending the MeTS/TMOS Ormosils series to $CH_3(CH_2)_2Si(OCH_3)_3$ (PrTS), $CH_2{=}CHSi(OCH_3)_3$ (ViTS), $(CH_3)_2CHCH_2Si(OCH_3)_3$ (^{i}BuTS), and $PhSi(OCH_3)_3$ (PhTS). Recent studies relevant to this report include the use of $E_T(30)$ and other polarity probes in several heterogeneous systems[8,9] and the use of doped Ormosils in several new optical sol−gel sensors.[1c,1e,10] Finally, we draw attention to another major strategy of controlling materials polarity, that is, through the entrapment of surfactants. For a recent application of that approach, see ref 11

Experimental Details

Chemicals. $Si(OCH_3)_4$ (TMOS), $CH_3Si(OCH_3)_3$ (MeTS), $CH_3(CH_2)_2Si(OCH_3)_3$ (PrTS), $CH_2{=}CHSi(OCH_3)_3$ (ViTS), and

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Table 1. λ_{max} and $E_T(30)$ Values of the Various Ormosils

	^{i}BuTS:TMOS		MeTS:TMOS		PhTS:TMOS		PrTS:TMOS		ViTS:TMOS	
molar ratio	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)
0.1:0.9	55.6	514	57.0	502	55.2	518	56.1	510	55.9	511
0.2:0.8	52.6	544	54.1	528	51.8	552	53.1	538	52.7	542
0.3:0.7	45.8	624	50.2	570	46.4	616	46.0	622	49.6	576
0.4:0.6	43.7	654	49.3	580	43.7	654	41.8	684	48.3	592
0.5:0.5	43.3	660	47.0	608	43.6	655	41.7	686	*a*	*a*

[a] The polarity for the 0.5:0.5 ratio was not characterized because a powder was obtained instead of a glass.

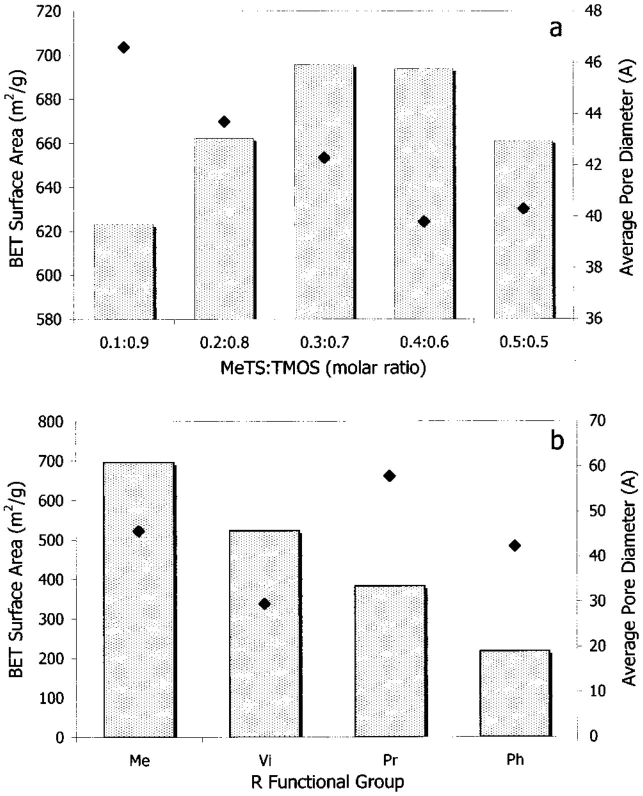

Figure 1. Surface areas (bars) and average pore sizes (dots) of the Ormosils: (a) as a function of composition for MeTS–TMOS; (b) as a function of the R group, for the molar composition RTS/TMOS = 0.3:0.7.

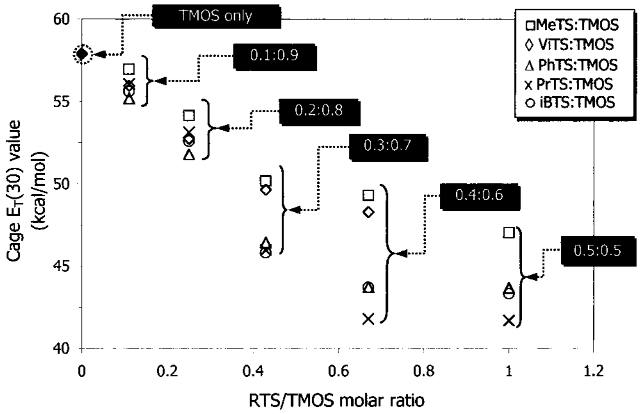

Figure 2. Polarity of the various Ormosils, in terms of $E_T(30)$ values, as a function of the R-group and of the composition.

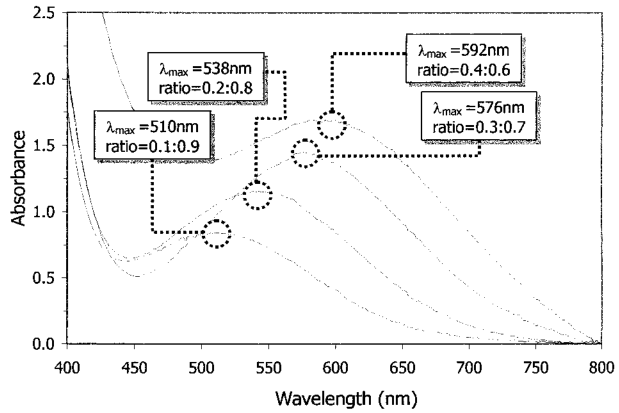

Figure 3. Effects of composition on the location of the absorption maximum of $E_T(30)$. Representative results are shown here for mixtures of ViTS–TMOS.

$(CH_3)_2CHCH_2Si(OCH_3)_3$ (^{i}BuTS) were from Aldrich, and $PhSi(OCH_3)_3$ (PhTS) was from Fluka. $E_T(30)$ was from Aldrich.

Doping Various Ormosils with $E_T(30)$. The standard molar ratio of components for all materials has been $E_T(30)$: water:MeOH:silanes = 5.3×10^{-4}:4.0:5.0:1.0 ($r = 4$), where "silanes" are composed of various monomers ratios as indicated in Table 1. A 2.25 mL volume of TMOS, the appropriate volume of silanes to keep the above ratio, 2.20 mL of MeOH, 0.8 mL of a 1% methanolic solution of $E_T(30)$, and 1.20 mL of water were sonicated for 5 min, after which 1.20 mL of water was added (to reach $r = 4$), and the mixture was sonicated for an additional 10 min. The mixture was allowed to gel at room temperature for 5 days and then dried for 2 days at 45–50 °C, followed by final drying for 24 h at 100–110 °C. The entrapment in pure silica sol–gel was described previously.[12]

$E_T(30)$-Value Determination. Matrix effects on the dopant were determined by visible-light spectroscopy (with a HP 8452A diode array spectrometer). For the study of interfacial solvent effects, the porous, transparent glasses were equilibrated with the desired solvent for 30 min prior to the measurements. The $E_T(30)$ value was calculated from the λ_{max} values according to[7]

$$E_T(30)(\text{kcal/mol}) = 28591/\lambda_{max}(\text{nm})$$

Surface Areas and Average Pore Sizes. These were determined from nitrogen adsorption/desorption data using a Micromeritics ASAP 2000 instrument. Typical BET surface areas and average BJH-pore diameters are collected in Figure 1: Figure 1a shows the data for MeTS/TMOS of various compositions, and Figure 1b takes one composition (RTS/TMOS ratio of 0.3:0.7) and shows the data for the various R's.

Results

The ability to fine-tune the polarity of the Ormosils either through the RTS/TMOS ratio or by varying R is clearly revealed in Figure 2 (see Table 1 for details and Figure 3 for representative spectra). The spectral changes in all the various glasses and the various compositions are reflected by a beautiful array of colors. The porous

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Table 2. Polarity Values of Several Solvents as Sensed by Ormosils Having the Molar Ratio RTS:TMOS = 0.5:0.5 (R = Me, Ph, Pr)

	MeTS:TMOS		PhTS:TMOS		PrTS:TMOS		neat solvent	
solvent name	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)
MeOH	54.4	526	53.3	536	55.0	520	55.5	515
EtOH	51.2	558	50.2	570	51.1	560	51.9	551
1-PrOH	50.5	566	49.3	580	49.8	574	50.7	564
2-PrOH	49.0	584	47.5	602	47.7	600	48.6	588
toluene	48.8	586	47.3	604	43.6	656	33.9	843

Table 3. Polarity Values for MeOH and EtOH as Sensed by the Ormosils MeTS:TMOS and PhTS:TMOS

	MeTS:TMOS (MeOH)		MeTS:TMOS (EtOH)		PhTS:TMOS (MeOH)		PhTS:TMOS (EtOH)	
molar ratio	$E_T(30)$ (kcal/mol)	$\Delta E_T(30)^a$ (kcal/mol)	$E_T(30)$ (kcal/mol)	$\Delta E_T(30)^a$ (kcal/mol)	$E_T(30)$ (kcal/mol)	$\Delta E_T(30)^a$ (kcal/mol)	$E_T(30)$ (kcal/mol)	$\Delta E_T(30)$ (kcal/mol)
0.1:0.9	57.9	2.5	53.6	1.7	56.9	1.5	53.1	1.2
0.2:0.8	56.9	1.5	53.1	1.2	54.4	1	52.0	0.1
0.3:0.7	55.8	0.4	52.2	0.3				
0.4:0.6	55.2	−0.2	51.8	−0.1	53.9	−1.5	50.3	−1.6
0.5:0.5	54.4	−1.1	51.2	−0.7	53.3	−2.1	50.2	−1.7

[a] $\Delta E_T(30) = E_T(30)_{glass} - E_T(30)_{solvent}$.

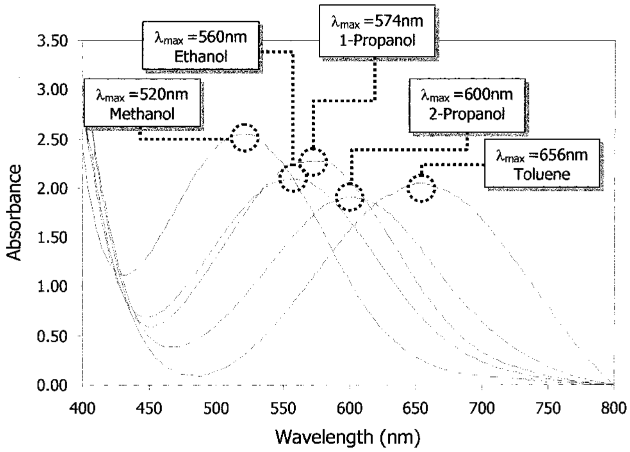

Figure 4. Effects of the interfacial and intracage solvent on the location of the absorption maximum of $E_T(30)$. Representative results are shown here for PrTS/TMOS = 0.5:0.5.

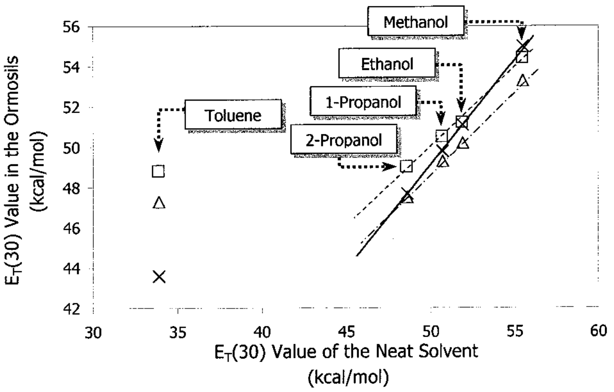

Figure 5. Correlation between the $E_T(30)$ of the solvents in the neat form and within the Ormosils. Materials symbols are as in Figure 2. Monomers molar ratio: 0.5:0.5.

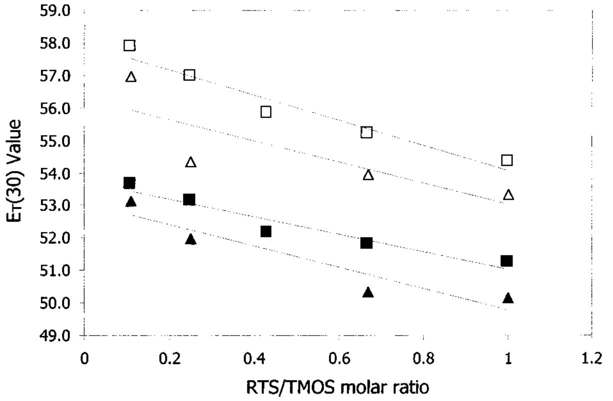

Figure 6. Ability of $E_T(30)$-doped MeTS:TMOS and PhTS:TMOS Ormosils to distinguish between methanol and ethanol, at various compositions. Shown is the $E_T(30)$ value (in kcal/mol) as a function of the molar ratio of the composition. Materials symbols are as in Figure 2: open symbols, methanol; closed symbols, ethanol.

interfaces of three $E_T(30)$-doped Ormosils (R = Me, Pr, and Ph, prepared at RTS/TMOS = 1/1) were exposed to five solvents: methanol; ethanol; 1-propanol; 2-propanol; toluene. Clear changes in the interfacial polarities were identified by the probe molecule and are collected in Table 2 (along with the $E_T(30)$ values of the neat solvents); representative spectra are shown in Figure 4. Comparison with the $E_T(30)$ values of the neat solvents is provided in Figure 5. The effects of changing the RTS/TMOS ratio on interfacial polarities were investigated for two R's, Me and Ph, and for two solvents, MeOH and EtOH, and the results are collected in Table 3 and in Figure 6.

Discussion

Our frame of reference will be the $E_T(30)$ values of several neat solvents (Table 2): The values range from 33.9 kcal/mol for the hydrophobic toluene, increasing up to 55.5 kcal/mol for the polar methanol. Another reference value is the polarity of pure silica sol−gel, which on the $E_T(30)$ scale was found to be 57.9 kcal/mol[12] (a maximum at 494 nm) and which indicates a polarity between water (63.1 kcal/mol) and methanol, somewhat closer to methanol. It is seen that $E_T(30)$ provides an unusually wide scale of polarity, spanning over more than 300 nm, which explains the popularity of that probe.

Returning to the dried Ormosils, we first note in Figure 1 that, as expected, variations in monomers ratio and in the R groups affect the surface area and the porosity. However, in the following discussion we concentrate not on these global characteristics but on the question, what does the probe molecule report about its immediate environment? Two trends are seen in Table 1 and in Figure 2: The first—the obvious one—is a decrease in apolarity as the RTS/TMOS ratio increases. Less obvious are the specific $E_T(30)$ values associated with that change. While at the low end of 0.1:0.9 the polarity of the matrix, which surrounds the probe molecule, is still high and resembles that of methanol, at the high-ratio end, the polarity resembles that of aromatic hydrocarbons. Interestingly, although cages of Ormosils are expected to be quite rich in R-residues (especially for small R's—see below), the resultant $E_T(30)$ values for the intermediate ratios are quite far from that of hydrocarbons. Thus, despite expectation, the cages seem to be rich with SiOH groups, in agreement with a similar proposition made by Spange et al. for surfaces.[9] The high $E_T(30)$ value reflects the preference of the probe molecule to reside near silanols, more than near the hydrophobic residues. In any event, the fact that the probe "reports" an intermediate polarity value, is an important indication of the homogeneity of the Ormosil on a molecular level: $E_T(30)$, which is known to respond to the sum of all its solvation−shell interactions, "sees" in its immediate environment within the Ormosil both SiOH groups and R groups; clustering of these residues would lead to either two peaks or to a substantial broadening of the indicating absorption maximum. Molecular homogeneity of Me-Ormosil was already proposed in ref 6. An explanation for the relative richness of the cages of the 0.5:0.5 Ormosils in silanols may be linked to the solvent of the polycondensation process, which apparently does orient silanols into the cage interface through hydrogen bonds with it.

The second trend seen in Table 1 and in Figure 2 is associated with R: For Me, Vi, and Pr, the hydrophobicities increase with the size of the substituent for all ratios. Perhaps unexpectedly, the larger ^{i}Bu and Ph indicate lower hydrophobicities than the Pr residue. We have already described in this journal[13] that long R moieties tend to be somewhat buried by the formation of micellelike structures of the hydrolyzed RTS monomers and small oligomers, and this adds to further enrichment of the interface with silanols. Another important result seen in Figure 2 is the differences in the R-concentration sensitivity of the Ormosils to polarity changes: Me, on which we have already reported[6] and which is commonly used for introducing hydrophobicity, is the *least* effective from this point of view, and the substituent of choice for that purpose is Pr. Following the work of Spange,[9] this apparently reflects the ability of the bulkier substituent to make it more difficult for the probe molecule to reach the surface silanols, at the same interfacial concentration of R's.

Next, let us analyze the interfacial polarities of the solvent-filled Ormosils. As seen in Figure 5 and Table 1 the 0.5:0.5-ratio materials report for the alcohol $E_T(30)$ values which are quite close to the neat-solvent values. Interfacial solvation of the probe molecule by alcohols is, therefore, efficient, and these materials can be used for sensing of these solvents, taking advantage of the clear color changes from one solvent to the next. The apolar toluene is an exception in this series, and the probe reports a blend of interactions with surface silanols and with these solvent molecules. Toluene/Ormosil is also the most sensitive to the size of the substituent: More silanols are available for interaction in the methylated surface than in the Pr-derivatized surface, as explained above. These mixed interactions bring the values of the Ormosil/toluene interface to a close proximity to the alcohols, and therefore only the Pr-Ormosils can be used safely as a sensor for this solvent.

As seen in Figure 6, the ability to distinguish methanol from ethanol is retained even by changing the RTS/TMOS ratio. This is so despite the fact that the $E_T(30)$ values which are close to those of the solvent itself for the 0.5:0.5 ratio gradually change to more polar values, which reflect the increasing contribution from hydrogen-bonding silanols.

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