Selective Sorption and Solvation in Dansyl-Labeled Poly(dimethylsiloxane) Networks Swollen in Binary Solvent Mixtures

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ABSTRACT: Poly(dimethylsiloxane) (PDMS) networks were fluorescently labeled with the 1-(dimethylamino)-5-naphthalenesulfonyl (dansyl) chromophore. The networks were prepared by end-linking silanol-terminated PDMS with a mixture of methyltriethoxysilane (MTES) and *N*-((triethoxysilyl)propyl)-dansylamide (DTES). The selective sorption behavior of these networks swollen in binary mixtures of 1,4-dioxane and a series of water and linear alcohols was studied. Refractometry and equilibrium swelling measurements were used to determine the amounts of PDMS and solvent components inside the swollen networks. We find that the cosolvency behavior of the solvent mixture depends on the alkyl chain length of the amphiprotic solvent. Steady-state fluorescence spectra of the dansyl compound dissolved in binary solvent mixtures are compared to the fluorescence of dansyl-labeled networks swollen with the same solvent mixture. Differences in emission energy are related to differences in the polarity of the solvation shells surrounding the dansyl moieties. The composition around the labeled cross-link junctions is compared with the bulk composition to determine spatial heterogeneity in the distribution of solvent and polymer molecules. We find that while dioxane is preferentially sorbed, the alcohols preferentially solvate the fluorescent moieties. Water has a tendency to cluster inside the networks that is stronger than its tendency to preferentially solvate dansyl.

Introduction

When an elastomeric network is put in contact with a solvent, the network polymer will have a tendency to mix with the solvent. The solvent that is absorbed by the network polymer will displace the polymer and swell the network. Networks that reach swelling equilibrium in a mixture of two solvent species cause a redistribution of the solvent species. There are two thermodynamic quantities that characterize the ternary phase equilibrium. First, the total sorption potential characterizes the expansion of the network polymer coils. Second, one of the solvent components may be preferentially sorbed. Due to preferential sorption, the composition of the solvent phase inside the swollen network differs from the composition of the initial solvent mixture prior to swelling. Preferential sorption thermodynamics have been studied for polymer solutions and networks,[1–9] but the microscopic nature of these phase equilibria is poorly understood. The microscopic structure and dynamics of PDMS networks swollen in a single solvent has been studied with fluorescence,[10] NMR,[11] and scattering techniques.[11–14]

The purpose of the present study is to investigate the structure of elastomeric PDMS networks in equilibrium with binary solvent mixtures. We determine spatial inhomogeneities in the solvent distribution inside PDMS networks swollen in a range of mixtures of 1,4-dioxane and amphiprotic solvents.

To achieve this, we label PDMS networks with a fluorescent probe molecule that gives information about the polarity of its local environment. We observe the steady-state fluorescence emission spectra as we expose the network samples to the different series of solvent mixtures. We correlate these fluorescence signals with emission of the fluorescent compound dissolved in the corresponding binary solvent mixtures. We determine whether the fluorescent moieties in the networks are equally accessible to all solvent species present in the swelling solvent mixture.

We prepared PDMS networks with 1-(dimethylamino)-5-naphthalenesulfonyl (dansyl) covalently bound to a small fraction of the cross-link junctions. The fluorescent dansyl moiety shows a strong solvatochromic shift of its maximum fluorescence emission energy as a function of the polarity of its environment. This property has resulted in the use of dansyl as a probe of the microenvironment in synthetic polymer systems in both static[10,15–19] and time-resolved fluorescence spectroscopy[20–22] and studies of biological systems,[23] self-organizing systems,[24] and surfaces.[25,26]

The fluorescence signal from dansyl in a multicomponent system can reflect preferential solvation. Preferential solvation occurs because the fluorescent moiety itself locally perturbs its environment, with one of the species preferentially going into the solvation shell of the probe. By observation of the stationary fluorescence spectra of *N*-((triethoxysilyl)propyl)dansylamide (DTES) in methanol/toluene mixtures, it was previously determined[10] that DTES shows significant preferential solvation by methanol, the more polar solvent. The emission energy is lowered as methanol displaces toluene from the solvation shell of the dansyl. Fluorescence from dansyl-labeled PDMS networks swollen to equilibrium in these solvent mixtures indicated preferential solvation of the dansyl moieties by both solvent species relative to the network chain segments. However, this conclusion remained speculative, since the exact composition of the mixed solvent phase inside the networks was not determined.

The binary solvents that we use in this study consist of nonpolar 1,4-dioxane mixed with a homologous series of amphiprotic solvents: water, methanol, ethanol, 1-propanol, and 1-butanol. Dioxane has approximately

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the same local polarity as PDMS chain segments,[1,10] which differs strongly from the amphiprotic solvents used in this work, but it is miscible in all proportions with them.

The current study is organized as follows. First, we measured the emission spectra of the dansyl dye in the swollen networks and dissolved in the corresponding solvent mixtures. Second, we obtained the volume fractions of the three components inside the swollen networks through a combination of gravimetry and refractometry measurements. Thus, we can determine preferential sorption and preferential solvation independently. If the solvent distribution inside the swollen elastomers is heterogeneous, the fluorescence emission energy will differ from the case where spatially homogeneous, stoichiometric mixing of the two solvent species and PDMS chain segments would occur in the solvation shell of the dansyl probes. In order to determine the nature of the spatial distribution of solvent molecules inside swollen labeled networks, we calculate the deviation of the observed fluorescence energy from ideal average fluorescence emission energy values.

Experimental Section

N-((Triethoxysilyl)propyl)dansylamide (DTES) was obtained from Hüls-Petrarch and was used without purification. DTES dissolved in *p*-dioxane was subsequently mixed volumetrically with varying amounts of water and alcohols to achieve 1.0×10^{-5} M solutions. All solvents were spectral grade quality from Aldrich with a specified water content less than 3 ppm and were used immediately upon opening without further purification. To confirm the concentration of DTES in the binary solvent mixtures UV–vis absorption spectra were obtained on a Varian Cary 3 UV–vis spectrophotometer in dual-beam mode against reference samples containing no model compound. For these measurements, we determined and subsequently used a molar extinction coefficient of 14 000. The pH of these DTES solutions was greater than 6 in all cases.

For network preparation hydroxyl-terminated PDMS (750 centistokes), methyltriethoxysilane (MTES) and tin octoate catalyst were all obtained from Hüls-Petrarch and were used without further purification. We used a Waters GPC (510 pump and 410 differential refractometer) with PDMS standards and toluene as the solvent, and found the number-average molecular weight of the PDMS to be 15 500 with a polydispersity index of 1.98. The PDMS was end-linked at room temperature using a mixture of trifunctional ethoxysilanes with an excess ratio of ethoxy groups per chain end of 2.50. A cross-linker mixture was prepared containing 99.9 mol % MTES and 0.1 mol % DTES, diluted in 40 vol % THF. This mixture was pipetted into PDMS. Then we added 2 wt % of catalyst solution, consisting of 50% tin octoate in methyl-terminated PDMS. Polyethylene embedding molds were filled with 2.5 mL of the uncured mixture. These samples were cured at room temperature under nitrogen for 48 h at a relative humidity of 15%, followed by 72 h under vacuum. The samples were swollen in THF for 72 h to extract all unreacted materials. Next, the THF was replaced by toluene to which methanol was progressively added to deswell the samples. The weight fraction of extracted materials was gravimetrically determined as $w_s = 0.065 \pm 0.005$. After extraction the networks were swollen again to equilibrium in THF, and we found that the volume fraction of polymer in the swollen network reached a value of $v_{2m} = 0.27 \pm 0.005$. All weighing was done on a Mettler A240 microbalance with an accuracy of 10^{-4} g. The sol fraction was analyzed by gas chromatography for MTES, using a Hewlett-Packard 5890A GC. It contained $(2-6) \times 10^{-4}$ M MTES in THF.

All binary solvent mixtures were prepared volumetrically, and their compositions were determined through refractometry. Refractive indices (n) were measured at a constant ambient temperature with a Fisher Scientific refractometer and were fit iteratively with polynomials as a function of vol % polar solvent to determine the composition of the mixture. The accuracy of the instrument was $n \pm 0.0001$. Experimental error margins in determining solvent compositions are discussed in the Results section.

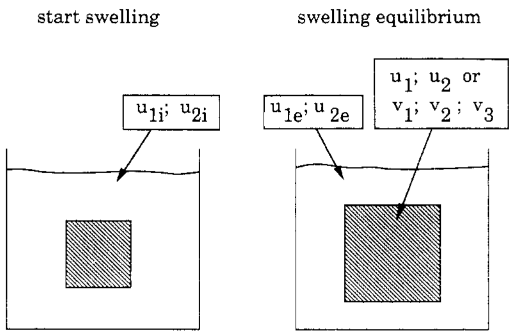

Figure 1. Schematic for nomenclature of volume fractions in the swelling experiment. Subscript 1 refers to dioxane, 2 to the amphiprotic solvent, and 3 to the polymer.

In the following we will employ standard nomenclature to indicate volume fractions of the three different components in each swelling experiment. This is illustrated in Figure 1. Prior to addition of the PDMS sample, the solvent mixture has an initial composition given by u_{1i} and u_{2i}, the volume fractions of solvent species 1 and 2, respectively. After the network has reached swelling equilibrium, we use v_j (j = 1, 2, 3) to indicate the volume fraction of component j within the swollen PDMS network. Alternatively, we use u_1 and u_2 to give the volume fractions of solvent species 1 and 2 in the binary solvent phase inside the swollen network, respectively. In addition, we use u_{1e} and u_{2e} to indicate the composition of the external solvent mixture that is in contact with swollen network at equilibrium conditions. In the fluorescence study of the DTES in solution we use x_j to indicate the volume fraction of solvent species j in the binary solvent mixture. In all cases, subscript 1 refers to dioxane, 2 to amphiprotic solvent, and 3 to the network polymer.

Extracted network samples were weighed and then swollen to equilibrium in a range of binary dioxane mixtures of known initial composition, expressed by u_{1i} and u_{2i}, referring to initial volume fraction of dioxane and amphiprotic solvent, respectively. After 48 h no more weight changes were observed. The swollen samples were then weighed in a closed vessel to determine the weight fraction of polymer and solvent phase in the swollen network.

After reaching an equilibrium extent of swelling, the refractive index of the residual solvent phase was measured and from this the composition was determined in terms of u_{1e} and u_{2e}, by comparison with a reference solution of known composition. In swelling equilibrium u_{1e} and u_{2e} are the volume fractions of dioxane and polar component, respectively, in the external solvent phase that is in contact with the swollen network. Given the weight fraction of solvent phase observed inside the swollen network, we could also determine the absolute amount of residual solvent as well as its composition.

The difference between the absolute amount of both solvent species in the external solvent phase, prior to and after swelling, has been taken up by the network. Given these amounts, the volumetric composition inside the swollen network was calculated: v_1 and v_2 are the volume fractions of dioxane and amphiprotic solvent, respectively, in the ternary system of the swollen network. We calculated the volume fraction of polymer in the ternary system as $v_3 = 1 - (v_1 + v_2)$. We also calculated u_1 ($\equiv v_1/(v_1 + v_2)$) and u_2 ($\equiv v_2/(v_1 + v_2)$), the volume fractions of dioxane and amphiprotic solvent in the binary solvent phase inside the swollen network.

Over a period of 6 months, we observed no aging effects in the series of networks swollen in water/dioxane. The emission spectra were constant, once swelling equilibrium was reached.

All steady-state fluorescence spectra were measured with a Spex Fluorolog 212 spectrometer. The network sample holder is described elsewhere.[10] The excitation source was a 450 W xenon lamp. Spectral resolution was held constant at

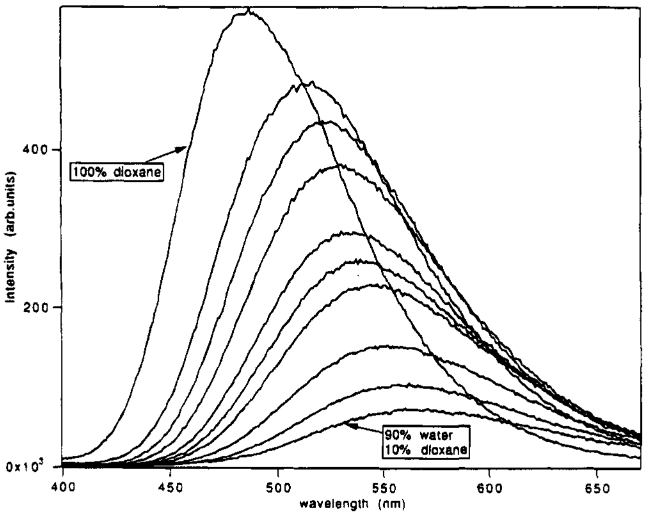

Figure 2. Fluorescence emission spectra obtained from 10^{-5} M DTES in binary mixtures of dioxane with varying volume fractions of water.

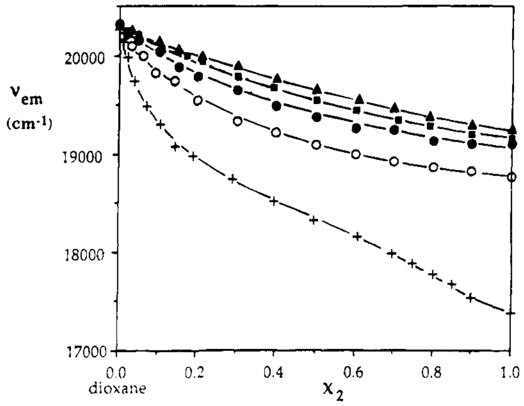

Figure 3. Fluorescence emission energy maxima, ν_{em}, of 10^{-5} M DTES in binary mixtures of dioxane with water and linear hydrocarbon alcohols as a function of x_2, the volume fraction of amphiprotic solvent: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

5 nm. All spectra were measured against a reference solution of Rhodamine-B in propylene glycol and were corrected for nonlinearities. In determining the center of gravity of the emission band in units of cm^{-1}, we corrected the spectra by a factor λ^2 for changes in the spectral resolution.

Results

Free DTES in Solution. Fluorescence emission spectra of low concentrations (10^{-5} M) of the DTES probe in binary solvent mixtures of 1,4-dioxane and amphiprotic solvents at room temperature show a broad emission band that red shifts strongly with increasing solvent polarity. In Figure 2, we show for example the emission spectra of 10^{-5} M DTES dissolved in dioxane/water mixtures. We determine the maximum energy of these emission spectra ν_{em} ($=\sum \nu I(\nu)/I(\nu)$, where $I(\nu)$ is the fluorescence intensity at energy ν) for DTES in all solvent mixtures of 1,4-dioxane and polar solvents. These maximum emission energies are plotted in Figure 3 as a function of x_2, the volume fraction of polar component in the solution. As can be seen in Figure 3, the maximum emission energy in pure polar solvents ($x_2 = 1.0$) increases monotonically over the water/linear alcohol series.

A monotonic decrease of maximum emission energy is observed as each polar solvent is added progressively to the dioxane solution. This indicates an increase in polarity of the solvent medium as it is probed in the immediate environment of the dansyl. By comparison, the absorption peak causing this radiative transition is relatively insensitive to solvent polarity. Only in the dioxane/water mixtures was a shift of the absorption peak observable, from 31 250 cm^{-1} for $x_2 = 0.0$ to 30 300 cm^{-1} for $x_2 = 1.0$.

In the current work we will be concerned only with the maximum energy of the emission band. An increase in polarity of the environment of the dansyl group also causes a decrease in the quantum yield of the fluorophore. However, integrated intensity data for swollen networks cannot be compared because the amount of fluorophores in the exciting beam varies strongly between samples due to thickness differences and differences in swelling.

The results in Figure 3 show that in all the binary mixtures of protic solvents with p-dioxane the emission energy of dansyl deviates from ideal, linear behavior; i.e., at intermediate composition ν_{em} is lower than the straight line connecting the $x_2 = 0$ and $x_2 = 1.0$ points, and thus the microenvironment is relatively more polar than in the ideal case. This deviation from linearity can be quantified by the nonlinearity ratio ϱ_{solv}, which is calculated in a simple numerical integration approximation:

$$\varrho_{solv} = \frac{(\nu_{em} - \nu_{em,lin})\Delta x}{(0.5\Delta\nu_{em,pure})} \tag{1}$$

where ν_{em} and $\nu_{em,lin}$ are emission maximum energies as observed and interpolated for linearity, respectively, $\Delta\nu_{em,pure}$ is the difference between the emission, in 12–15 increments for each solvent pair. In the case of complete linearity, $\varrho_{solv} = 0$, and in the case of infinite deviation from linear additivity, $\varrho_{solv} = 1$. The results for the emission energies are shown in Table 1. The deviation from linearity decreases as the substituent group on the hydroxyl changes from H to CH_3 to longer alkyl chains.

Table 1. Nonlinearity Ratios (ρ_{solv}) of DTES Maximum Fluorescence Energies in Binary Dioxane Mixtures (from Eq 1)

polar solvent	ρ_{solv}	polar solvent	ρ_{solv}
water	0.289	1-propanol	0.088
methanol	0.220	1-butanol	0.056
ethanol	0.155		

One possible cause of preferential solvation in binary solvent mixtures is the effect of "dielectric enrichment".[27] During the lifetime of the excited state of the probe, its increased dipole moment leads to "enrichment" of the solvation shell as the more polar solvent species that diffuse toward the probe remain in the electric field of the excited probe. As a result, the excited fluorophore experiences on average a more polar microenvironment than the bulk composition. Hence, a lower emission energy is observed than would be expected from the bulk composition. In a continuum model proposed by Suppan,[27] the nonlinearity ratio ϱ_{solv} of ν_{em} is proportional to the ratio between mole fractions of the polar and nonpolar solvent in the bulk liquid and the same ratio in the solvation shell around the probe. The solvatochromic shift of dansyl fluorescence emission is dependent on bulk solvent properties (ϵ, n) according to the Lippert equation.[28] Therefore, in order to quantify the deviation of the composition of the dansyl solvation shell from the bulk, using the fluorescence emission energy as an indicator, the nonlinearity in the dielectric polarizabilities of the bulk mixtures without the solute would have to be taken into account.[27]

Dielectric enrichment is a local nonspecific solute-induced association effect. Preferential solvation is a more general effect including dielectric enrichment and also specific associations such as hydrogen-bonding. Specific associations are possible, but it has been pointed out[10,29] that they play a relatively minor role in the solvent effects on fluorescence of substituted aminonaphthalenes.

Network Swelling. The PDMS networks were swollen to equilibrium in limited volumes of binary dioxane mixtures of known composition, and the volume fraction of polymer in the swollen networks (v_3) was determined as described in the Experimental Section. From swelling measurements in the pure solvents, we obtained values for χ_{j3}, the interaction parameter between the PDMS and pure solvent *j*. We based our calculations[30] on a perfect phantom network assumption, with M_c, the molecular weight between cross-links, being equal to M_n. The results are listed in Table 2.

Table 2. Volume Fraction of Polymer in Swollen Network (v_3), Binary Interaction Parameters between Solvents and PDMS Networks Based on Phantom Network Calculations (χ_{i3}), and Literature Values of Hildebrand's Solubility Parameter (δ, from Barton)

solvent	v_3	χ_{3i}	δ ($J^{1/2}$ $cm^{-3/2}$)
dioxane	0.722	1.07	20.5
water	0.995	4.32	47.9
methanol	0.983	3.18	29.6
ethanol	0.934	2.05	26.0
1-propanol	0.841	1.41	24.3
1-butanol	0.827	1.36	23.3

The χ-values for these five solvents are high relative to most other solvents in PDMS.[31] This is to be expected for the amphiprotic solvents. However, dioxane is not a particularly good swelling solvent for PDMS compared to THF ($\chi = 0.452$ for PDMS of $M_n = 17\,200$[31]) or diethyl ether ($\chi = 0.4$[31]), although the polarity of each of these three ethers resembles that of PDMS.[30] This is another indication of the high local polarity of dioxane relative to its bulk dielectric properties. Previously, the equation-of-state χ for dioxane–PDMS obtained at infinite dilution from inverse GC was 1.32 at 25 °C.[31] The difference with our calculated result of $\chi = 1.07$ is due to self-condensation of the cross-linking precursor,[32] which results in higher cross-link functionality. In addition, at low extents of swelling the phantom network limit is not reached.[33] For alkanes it has been found[7] that the thermodynamic quality of these solvents for PDMS is inversely proportional to their alkyl chain length, but the opposite effect is found for the linear alkyl alcohols of low molecular weight used in the present study.

Figure 4 shows v_3, the volume fraction of polymer in the swollen network, as a function of u_{2i}, the volume fraction of the polar component in the initial swelling mixtures. The dependence of v_3 on u_{2i} is related to ΔG^E, the excess Gibbs free energy of mixing of the two solvent components in a nonideal solvent mixture.[16,23,24]

$$\Delta G^E = \Delta G_m - RT\sum x_j \ln x_j \qquad (2)$$

where ΔG_m is the actual Gibbs free energy of mixing and the summation gives the Gibbs free energy of mixing for an ideal mixture. Cosolvency is an increase in solubility at intermediate solvent compositions relative to the linear dependence of v_3 on the composition of the binary solvent phase, u_{2i}. Cononsolvency is a decrease in solubility; the two solvent components are good solvents relative to the solvent mixture, which is a nonsolvent.

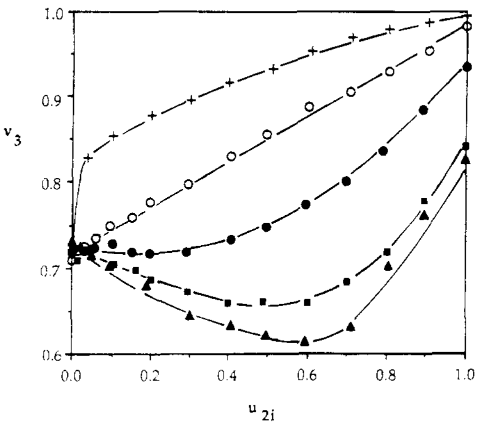

Figure 4. Volume fraction of polymer in the swollen networks, v_3, as a function of u_{2i}, the volume fraction of polar solvent in the initial swelling liquid: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

Figure 4 shows that for the solvent pair dioxane/methanol the swelling behavior of PDMS is approximately a linear function of u_{2i}. This indicates that ΔG^E is zero.[3] In the case of dioxane/water/PDMS, the total sorption is strongly decreased by adding a small amount of water to dioxane in the swelling mixture. This cononsolvency effect corresponds to a favorable interaction between the two liquids, $\Delta G^E < 0$, which leads to segregation of the polymer due to the solvent and, hence, to the deswelling of the network.[3,9] For ethanol, 1-propanol, and 1-butanol in dioxane the total swelling of the network is increased at intermediate compositions relative to ideal swelling behavior. In these cases the interactions between the two solvent species are unfavorable, i.e., $\Delta G^E > 0$: segregation of the solvents leads to enhanced solubility of the polymer. The absolute value of ΔG^E appears to increase with alkyl chain length.

In thermodynamic equilibrium the chemical activity of the two solvent species is the same in the ternary phase (the swollen PDMS network) as in the binary swelling phase with which it is in contact. The solvent species in the ternary system that has the most favorable interaction with the PDMS is preferentially sorbed. The result of preferential sorption is shown in Figure 5, where the volume fraction of polar component in the solvent phase inside the swollen elastomers, u_2, is plotted as function of the volume fraction of polar component in the initial swelling mixture, u_{2i}. Dioxane is preferentially sorbed from all swelling mixtures. Minima in v_3 in other ternary systems have often been related to inversion in preferential solvation,[4,9] although the absence of inversion we observe here has also been identified in other systems.[2] The longer the hydrocarbon tail on the alcohols, the weaker the effect of preferential sorption, i.e., the closer u_2 is to u_{2i}.

In the dioxane/water mixtures, determination of compositional changes in the internal solvent phase was subject to an error, because the total quantities of swelling solvent residing in the network are relatively small. In all the other mixtures a significant error was also introduced as the differences in refractive index between dioxane and the alcohols become smaller in going from methanol to butanol. As a result, the

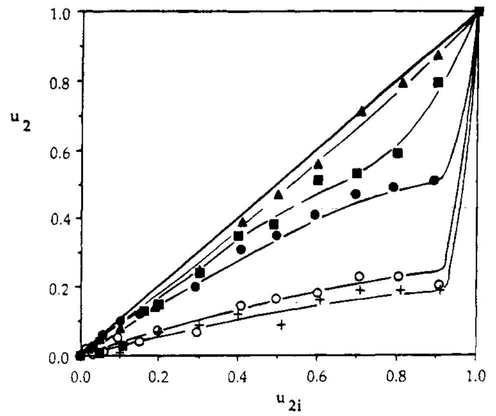

Figure 5. Composition of the binary liquid phase inside the swollen networks, u_2, as a function of u_{2i}, the volume fraction of polar amphiprotic solvent in the initial swelling liquid: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

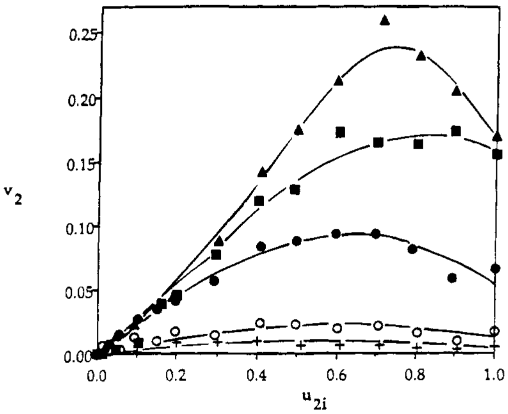

Figure 6. Volume fraction of polar solvent in the ternary system, v_2, as a function of u_{2i}, the volume fraction of polar solvent in the initial swelling mixture: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

uncertainty in the values of v_1 and v_2 varies from ±2% in dioxane/butanol/PDMS up to ±5% in dioxane/water/PDMS.

The maximum absolute amount of polar solvent component is sorbed at solvent compositions of intermediate polarity, as shown in Figure 6. The presence of dioxane enhances the uptake of ethanol, propanol, and butanol, although dioxane is preferentially sorbed. Comparison of Figure 4 with Figure 6 shows that these maxima in v_2 do not coincide with minima in v_3, the volume fraction of polymer in the swollen system.

Fluorescence of Dansyl Bound to Cross-Link Junctions in Swollen Networks. After the labeled networks reached swelling equilibrium, their fluorescence emission spectra were obtained. The observed emission maxima ν_{em} are shown as a function of u_{2i} in Figure 7. The most striking feature of this figure is the difference between the fluorescence from the dioxane/water/PDMS and the dioxane/alcohol/PDMS systems. In the dioxane/water-swollen networks ν_{max} is much higher; i.e., the polarity of the solvation shell surrounding the dansyl moieties is much lower than in any ternary systems with the alcohols. The fluorescence from networks swollen in pure alcohols ($u_{2i} = 1$) does not show a clear trend with alkyl chain length of the alcohols. In addition, in the ternary systems with alcohols, different trends are observed. In the systems dioxane/propanol/PDMS and dioxane/butanol/PDMS, ν_{em} decreases monotonically with u_{2i}, so the polarity of the environments of the dansyl groups increases with u_{2i}. In the networks swollen in dioxane/methanol and dioxane/ethanol mixtures, ν_{em} is constant for values of u_{2i} greater than 0.5 and 0.8, respectively.

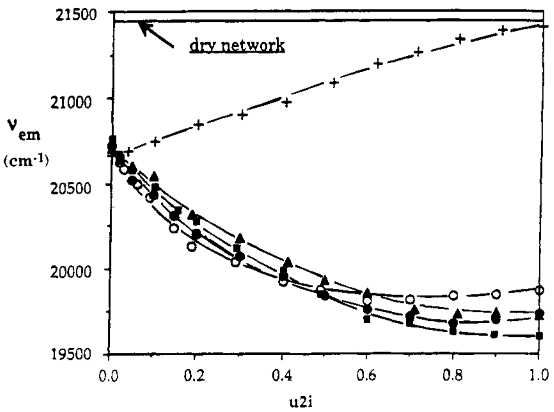

Figure 7. Observed fluorescence maximum energy of dansyl-tagged PDMS networks swollen in binary mixtures, ν_{em}, as a function of u_{2i}, the volume fraction of polar solvent in the initial swelling liquid: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

Discussion

Fluorescence of Free DTES in Solution. A number of attempts have been made at explaining the photophysical behavior of substituted aminonaphthalenes[34-37] and of dansyl[23,38] in solution. The general solvatochromic effect can be explained in terms of a dielectric relaxation mechanism. The excited state of the π^*-orbital of dansyl has a higher dipole moment than the ground state; this leads to reorientation of the solvent dipoles around it, thus lowering the energy of the emitting state.[28] Dansyl is thought to experience significant twisted intramolecular charge transfer (TICT) character in the ^1L_a excited state as the lone-pair electron on the amino group transfers into the π^*-orbital of the naphthalene ring.[35] This charge transfer is enhanced by the electron-withdrawing sulfonyl group, resulting in the relatively large excited-state dipole moment.[23,38] The picture may be complicated by mixing of the ^1L_a/charge transfer state and the ^1L_b state, which is dependent on solvent polarity, resulting in inversion of these energy levels.[38]

In the bulk solvent mixtures the amphiprotic solvents both self-associate and act as hydrogen-bond donor species to form complexes with the dioxane, which has oxygens acting as hydrogen-bond acceptors and electron pair donors. The excess Gibbs free energy of mixing ΔG^E is positive for all these binary solvent mixtures (calculations based on Gmehling's data[39]). The liquid state structure of mixtures of dioxane and the hydrogen-bond donating solvents has been studied by a number of groups, using techniques such as microwave dielectric spectroscopy,[40] the solvatochromic absorption shift of E_T-30,[41] and magneto-optical rotation.[42] In all of these studies, discontinuities in the relevant properties are observed, with a critical point occurring at an intermediate composition. Below the critical dioxane concentration, water forms cyclic clusters, and alcohols form chainlike clusters. Above these concentrations, the result of adding dioxane is to decrease specific interactions and therefore to disrupt the structure in these solvents.

The current fluorescence results of DTES show that the emission energies are smooth functions of volume fraction of polar solvent. There are no discontinuities related to the expected structure breaking action of dioxane in the polar solvents in the curves of Figure 3. This suggests that the fluorescence from DTES is indicative of the polarity of the solvent mixtures rather than their structure. This is in agreement with the suggestion of Reeves et al.[29] that the contribution to the frequency shift from solvent cohesion should be relatively small for aminonaphthalenesulfonates compared to the anilinonaphthalenesulfonates (TNS): specific interactions between solute and solvent play only a minor role in the solvent effects affecting the emission energy of DTES as opposed to TNS in aqueous alcohols. On the other hand, Ghiggino et al.[23] observed that the TICT efficiency does depend on solvent viscosity and coherence, such that strongly structured polar solvents would hinder TICT by sterically hindering conformational reorientation of the dimethylamino substituent. We calculated values of Hildebrand's solubility parameter δ of different water/dioxane mixtures (based on Stallard's[43] and Barton's[31] data) but found only a weak correlation of δ with our observations of ν_{em} in these systems. For the other mixtures no literature values of the molar enthalpy of vaporization were available and therefore we could not correlate δ with ν_{em} for those cases.

The ν_{em} of DTES in dioxane is relatively high for its δ compared with the general trend in a wide range of solvents.[10] We suggest two possible reasons to explain why the apparent local polarity of dioxane is high relative to its bulk dielectric polarizability. First, the DTES may only probe part of the dioxane molecules and hence regard dioxane as having a dipole. Second, the predominant dioxane conformation in bulk solution is the chair conformation[44] with no associated net dipole, whereas dioxane near a polar solute may assume a boat conformation with a significant dipole. In addition to dielectric enrichment effects, these two orientational effects may influence dansyl fluorescence in dioxane mixtures.

Network Swelling. In the swollen networks, random mixing of the network polymer with the solvent phase cannot be assumed and thermodynamic properties have to be derived from equilibrium constants for association. Preferential sorption depends on the molar volume of the solvent species as well as on the ternary interaction parameters.[2,3,5,6] However, deriving these parameters is beyond the scope of the current study. We will consider the results from the swelling experiments, distinguishing three types of solvency behavior of the solvent mixtures based on Figure 4.

We first consider the dioxane/water/PDMS mixtures. Based on the swelling results, one would conclude that $\Delta G^E < 0$ for the corresponding dioxane/water mixtures. This is in contradiction with literature values.[39] A very strong unfavorable interaction between water and PDMS exists as indicated by the high χ_{13} for this system in Table 2. These interactions between water and PDMS chain segments lead to nonrandom mixing: water aggregates form phase-separated clusters.[45-47] The water molecules interact through hydrogen bonding in the highly mobile PDMS matrix, and the higher the water concentration, the more important the clustering process becomes.

The second group to consider is the series dioxane/methanol/PDMS. Swelling of networks corresponds to linear interpolation of the two pure compounds, indicating $\Delta G^E = 0$. This is also in disagreement with ΔG^E values calculated from literature data.[39] Methanol has been found to cluster in PDMS elastomers as well.[48]

The third group consists of PDMS swollen in the mixtures of dioxane with ethanol, 1-propanol, or 1-butanol. All of these mixtures show cosolvency behavior toward the networks, corresponding to $\Delta G^E > 0$, in agreement with literature values for the binary liquids.[39]

The above three distinct modes of swelling behavior indicate that ΔG^E is not the only parameter governing solvent distribution and preferential sorption. If the 1−3 (dioxane/PDMS) and the 2−3 (amphiprotic solvent/PDMS) contacts in the ternary systems are lower in energy than in the binary (solvent/PDMS) systems, the polymer solubility will increase and hence v_3^{-1} can be expected to be higher. Cosolvency is attributed primarily to the enthalpic part of the polymer-mixed solvent interaction parameter.[9] Solvent species that do not compete for the same site on the polymer chain tend to form cosolvent pairs and vice versa. Hence, we propose that in the ternary systems, the amphiprotic solvents solvate the PDMS chains at different sites depending on the alkyl chain length. The Si−O backbone of PDMS is partly polar in nature, but is enveloped by a sheath of nonpolar methyl groups.[49,50] Water and methanol compete with dioxane for the same solvation sites on the PDMS while the longer alcohols interact with PDMS at other sites than the dioxane. However, we cannot make additional statements about the nature of the polymer−solvent interaction sites based on our swelling observations alone.

Fluorescence of Dansyl Bound to Cross-Link Junctions in Swollen Networks. In this part of the discussion we will address the solvent distribution phenomena in swollen networks using our fluorescence emission results in addition to the above thermodynamic considerations. The concentration of the probe is so low that it has negligible influence on the position of ternary equilibria, but locally the dansyl moieties cause a heterogeneity in their solvation shell through dielectric enrichment. Therefore, their emission energy is not an indicator of preferential sorption in the domain of the unlabeled cross-links.

If the dansyl moieties are equally accessible to all species in the swollen systems (two solvent species and the network polymer) and the solvent distribution is spatially homogeneous, then we can expect different emission energies than when the solvent is distributed heterogeneously with respect to the labeled cross-link junctions. However, homogeneous mixing of the three components in the solvation shell of the dansyl moities is a hypothetical state. We derive hypothetical emission energies that could possibly result from homogeneous mixing, using three different averaging procedures. Subsequently, we compare our emission results to these hypothetical average emission energies. If the differences are large, we assume that the composition of the actual solvation shells is far from the average composition of the ternary systems.

We first consider the possibilities for inhomogeneous distribution. If, in a swollen network, solvent molecules remain away from the labeled cross-links, they will not be probed by the immobilized dansyl moieties during the excited-state lifetime and the emission energy will be relatively high. If the solvent associates with the dansyl moieties, this will produce a relatively polar dynamic local environment and, hence, the emission peak will be red-shifted. If, on the other hand, there would be no spatial heterogeneities, both the solvent species and the network polymer would solvate each dansyl moiety proportional to their respective volume fractions that we actually measure in the swollen network. The polarity of the solvation shell and, therefore, the resulting fluorescence emission energy would be an average. In the following we will calculate this average emission energy in three different ways and interpret the deviations of the observed emission energy.

First, we can approximate the average polarity that the dansyls probe as the contribution of each species j, weighted by their volume fraction v_j. This "volumetric mixing" of energies results in an average emission energy:

$$\nu_{\mathrm{vm}} = v_1\nu_{\mathrm{diox}} + v_2\nu_{\mathrm{ROH}} + v_3\nu_{\mathrm{PDMS}} \qquad (3)$$

where ν_{diox}, ν_{ROH}, and ν_{PDMS} correspond to the fluorescence emission energies in pure dioxane, ROH, and the dry network, respectively. Deviations of the observed emission energy from this average could be attributed either to preferential solvation or to nonrandom solvent distribution. Using this approach, we cannot discriminate between these two effects. Therefore it is not useful for determining solvent distribution.

An alternative averaging approach is the following. The fluorescence energies in a homogeneous mixture could be the averages of the fluorescence energies of networks swollen in pure dioxane and pure amphiprotic solvent, weighted according to volume fractions u_1 and u_2, respectively. The average emission energy resulting from this "mixing" of fluorescence energies is calculated as

$$\nu_{\mathrm{mfe}} = u_1\nu_{\mathrm{PDMS/diox}} + u_2\nu_{\mathrm{PDMS/ROH}} \qquad (4)$$

where $\nu_{\mathrm{PDMS/diox}}$ and $\nu_{\mathrm{PDMS/ROH}}$ are the maximum emission energies of dansyl in tagged PDMS networks swollen in pure dioxane and pure amphiprotic solvent, respectively. The problem with the use of eq 4 is twofold. It does not account for preferential solvation of dansyl by the polar component of the binary solvent phase inside the network. In addition, since v_3 does not enter eq 4, it does not account for co(non)solvency effects, either.

In order to account for both effects, we consider a third hypothetical case, where stoichiometric binary mixing of the network polymer and the solvent phase would occur. Each of the fluorescent moieties is solvated by a binary mixture of the network polymer and the solvent phase, in proportion to their respective volume fractions, v_3 and $(v_1 + v_2)$. Within the solvent phase, the polar solvent preferentially solvates the dansyl to the same extent as it solvates DTES in solution. We can calculate the corresponding average resulting from this "binary mixing" of emission energies as

$$\nu_{\mathrm{bm}} = v_3\nu_{\mathrm{em,PDMS}} + (v_1 + v_2)\nu_{\mathrm{em,sol}} \qquad (5)$$

where $\nu_{\mathrm{em,PDMS}}$ is the emission energy of dansyl in the dry network and $\nu_{\mathrm{em,sol}}$ the emission energy of the model compound in the binary solutions for the composition x_2 corresponding to the composition u_2 of the binary solvent phase inside the swollen network. We find the value of $\nu_{\mathrm{em,sol}}$ directly from Figure 3.

We plot ν_{bm}, the fluorescence emission energy that would result from such an ideal mixture, as a function of $u_{2\mathrm{i}}$ in Figure 8. Five regularly spaced curves result that differ strongly from our experimental observations of ν_{em} plotted as a function of $u_{2\mathrm{i}}$ in Figure 7.

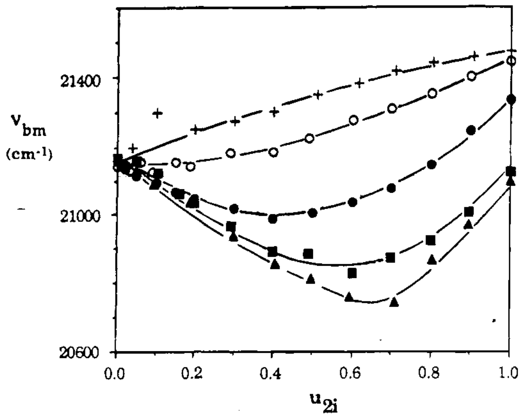

Figure 8. Hypothetical emission energies ν_{bm} calculated for the hypothetical case of volumetric binary mixing of the solvent phase and chain segments in the solvation shells of the bound probes in swollen PDMS networks according to eq 5 plotted as a function of $u_{2\mathrm{i}}$, the volume fraction of polar solvent in the initial binary swelling mixture: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

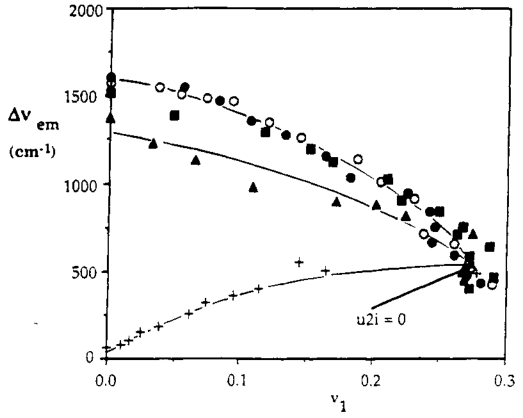

Figure 9. $\Delta\nu_{\mathrm{em}}$, from eq 6, the difference between ν_{em} from swollen PDMS networks and ν_{bm}, the hypothetical maximum emission energies calculated for the case of volumetric binary mixing of the solvent phase and chain segments in the solvation shells of the bound probes, plotted as a function of v_1, the volume fraction of dioxane in the ternary phase: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

The difference between ν_{bm} from eq 5 and the observed fluorescence energy is called $\Delta\nu_{\mathrm{em}}$:

$$\Delta\nu_{\mathrm{em}} = \nu_{\mathrm{bm}} - \nu_{\mathrm{em}} \qquad (6)$$

This quantity is shown as a function of v_1 in Figure 9 and as a function of v_2 in Figure 10. If "stoichiometric" mixing (spatially homogeneous solvent distribution) would occur in all the swollen systems, then all the values of this energy difference would be zero at each measured v_1 and v_2. The values of $\Delta\nu_{\mathrm{em}}$ that we find are positive in all systems, so the actual emission energy is lower than expected based on eq 5. This indicates a relatively polar solvation shell compared to the average polarity in eq 5. Thus, $\Delta\nu_{\mathrm{em}}$ can be used as a measure for the extent of preferential solvation. When $\Delta\nu_{\mathrm{em}}$ is far from zero, the composition of the solvation shells is far from the average composition of the ternary system. In the rest of this Discussion section, we elaborate on this point.

First, we consider $\Delta\nu_{\mathrm{em}}$ in the binary systems of networks swollen in pure solvents (v_1 or $v_2 = 0$). The system dioxane/PDMS ($v_2 = 0$ in Figure 10) has a lower ν_{em} than predicted by eq 5, indicating a more polar solvation shell of the dansyl. This suggests that dioxane

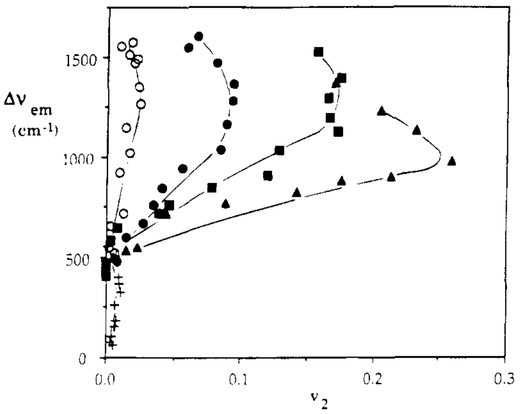

Figure 10. $\Delta\nu_{em}$ plotted as a function of v_2, the volume fraction of polar solvent in the ternary phase: (+) water; (○), methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

displaces PDMS chain segments from the environment of the probes, possibly due to its higher local polarity.

For the four binary alcohol/PDMS systems ($v_1 = 0$ in Figure 9), $\Delta\nu_{em}$ is much larger than for dioxane/PDMS. This suggests that the polymer is displaced much more strongly from the dansyl solvation shells by the alcohols than by dioxane. The deviation $\Delta\nu_{em}$ is approximately the same for all four alcohol-swollen networks at $v_1 = 0$ in Figure 9. According to Figures 4 and 10, though, v_2 does depend on alcohol chain length when $v_1 = 0$. Thus, the length of the alkyl group on the alcohols only has an influence on their solubility in PDMS, not on the way they displace PDMS from the solvation shells of the dansyls. This may indicate that the polar head group of the alcohol interacts favorably with polar dansyl while its alkyl chain interacts with the methyl on PDMS chain segments, keeping those segments away from the probe.

The deviation $\Delta\nu_{em}$ for water/PDMS at $v_1 = 0$ is relatively small. If water would displace PDMS from the solvation shells of the probes, then a large $\Delta\nu_{em}$ would result, similar to those observed in the PDMS/alcohol systems. We explain the small $\Delta\nu_{em}$ as follows: the tendency of water to self-associate and thus minimize water/PDMS interactions is stronger than its tendency to cluster around the polar probes, which would still involve high-energy interactions with the hydrophobic matrix.

The second step in interpreting our $\Delta\nu_{em}$ is to consider systems of ternary composition, where v_1 and $v_2 \neq 0$. A strong contrast exists between the dioxane/water and the dioxane/alcohol systems in Figures 9 and 10. Apparently, the nature of the polar solvent species is important in determining the amount of preferential solvation. We will discuss first the water and then the alcohol mixtures.

For the dioxane/water/PDMS systems in Figure 9, $\Delta\nu_{em}$ increases monotonically with increasing v_1. Preferential solvation of the bound dansyls increases with the volume fraction dioxane. In Figure 10 we see that in these systems, $\Delta\nu_{em}$ is not proportional to v_2. We attribute the change in $\Delta\nu_{em}$ in these systems to the replacement of PDMS by dioxane in the dansyl solvation shells.

In Figure 9 we see for dioxane/alcohol/PDMS systems that, within the experimental error, the effect of increasing v_1 is approximately the same for these solvent pairs. As v_1 increases, the volume fraction of alcohol decreases and $\Delta\nu_{em}$ decreases monotonically, suggesting that the alcohol molecules are depleted from the solvation shells of the dansyl groups in the same fashion in these systems.

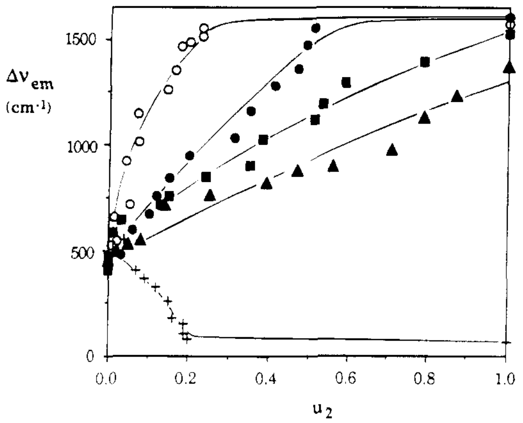

Figure 11. $\Delta\nu_{em}$ plotted as a function of u_2, the volume fraction of dioxane in the binary solvent phase inside the swollen network: (+) water; (○) methanol; (●) ethanol; (■) 1-propanol; (▲) 1-butanol.

In Figure 10, on the other hand, the magnitude of the effect of changing v_2 is dependent on the alcohol species. In all alcohol systems with ternary composition, $\Delta\nu_{em}$ is intermediate with respect to $\Delta\nu_{em}$ from the networks swollen in the pure solvents (v_1 or $v_2 = 0$). However, for these systems we observe a nonmonotonic behavior of v_2 in Figure 10. This is directly related to Figure 6: the maxima in v_2 correspond to $u_{2i} \approx 0.7$ for all four dioxane/alcohol series. For those parts of the curves in Figure 10 that have a positive slope, an increase of v_2 enhances the preferential solvation of dansyl by the alcohols. To explain the parts of the curves that have a negative slope in Figure 10, we suggest that this increase in $\Delta\nu_{em}$ with decreasing v_2 is due to replacement of dioxane by the more polar alcohol species in the dansyl solvation shells.

The above suggests that preferential solvation in all systems is correlated more strongly with u_2 than with v_2. This is confirmed by Figure 11, where we plot $\Delta\nu_{em}$ as a function of u_2. In the water/dioxane systems we see a negative slope in Figure 11. As water replaces dioxane in the solvent phase, the emission energy gets closer to that of the dry network. This confirms our conclusion that water forms clusters away from the labeled cross-links. Increasing u_2 from 0.2 to 1.0 has no effect on preferential solvation; $u_2 = 0.2$ appears to be a saturation level.

For all four alcohol species, we see a positive slope in Figure 11. An increase of u_2 corresponds to an increase in preferential solvation: alcohol molecules displace both the dioxane and the network chain segments. The shorter the alkyl chain, the steeper the slope, and thus the stronger the dependence of $\Delta\nu_{em}$ on u_2. The nature of the preferential solvation of the bound probes is roughly the same for these alcohols, although the volume fraction u_2 that causes some extent of preferential solvation depends strongly on the length of the chain on the alcohol.

Finally, the spatial distribution of solvent molecules is related to the dry network morphology. We prepared a batch of end-linked networks with a constant structure, containing, however, various structural imperfections.[51] We observe that the emission energy of dansyl bound to cross-link junctions in dry networks (21 480 cm^{-1}) is higher than the DTES model compound emission energy in 1000 cP trimethylsiloxy-terminated PDMS (21 240 cm^{-1}), indicating a slightly higher local polarity. One plausible cause for this is clustering of triethoxysilanes during network formation,[32] which may impose configurational limitations on the environment of the dansyl-tagged cross-links or may even bring dansyl moieties into each other's solvation shell. A discrepancy between the observed and predicted weight fraction extractables for end-linking reactions indicates that the cross-linking precursor molecules homopolymerize to a significant extent. This self-condensation of silanes may result in cross-link structures that put additional steric constraints on the accessibility of the dansyls to solvent molecules and polymer segments. Other network imperfections in the form of unreacted siloxane chain ends or hydrolyzed silanes, both giving polar silanols, possibly result in a local environment of high polarity that interacts favorably with the polar solvent species, thus creating localized pools of polar solvent.

Concluding Remarks

In this paper we have shown that dansyl moieties covalently bound to the cross-link junctions in PDMS elastomers have varying accessibility for different solvent species that swell the network. The fluorescence emission signals from these labeled networks are not sufficient to distinguish the type of polar solvent that is present in a dioxane. However, these networks can be used to probe the amount of a known polar solvent in such a mixture.

In swelling experiments the PDMS networks preferentially sorb dioxane from all binary mixtures with polar solvent. The cosolvency character of the mixed systems increases with alkyl chain length on the linear alcohols. We argue that dioxane competes with water for similar interaction sites on the polymer chain but interacts at different sites on the PDMS chains than ethanol, 1-propanol, and 1-butanol.

From fluorescence emission spectroscopy we obtain information about the composition of the solvation shell of dansyl moieties that are bound to the cross-link junctions. Water self-associates in clusters through hydrophobic interaction with PDMS. These water clusters are spatially distributed away from the cross-link junctions and they do not compete with dioxane for uptake in the solvation shell of the network-bound dansyl.

Both dioxane and alcohol molecules displace network chain segments from the local environment of dansyl-tagged cross-links in swollen networks. Preferential solvation of these immobilized dansyl groups by alcohols is stronger than by dioxane.

Preferential solvation of the free dansyl compound in binary dioxane solutions containing linear alcohol decreases with increased alkyl chain length. On the contrary, in the swollen networks, the influence of the alcohol on the preferential solvation of bound dansyl appears independent of alkyl chain length.

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