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The Photoluminescence of Poly(methylphenylsilylene). The Origin of the Long-Wavelength Broad Band

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ABSTRACT: The photoluminescence of poly(methylphenylsilylene) consists of a relatively sharp band at 350 nm and a significantly broad band in the 400–500-nm region. The luminescence behavior is investigated at low temperatures in an effort to identify the origin of the long-wavelength broad emission. The excitation spectra differ for the sharp and the broad emission bands: The broad emission band is more enhanced when the excitation is carried out at the π,π^* absorption band of the phenyl substituent as compared to the excitation at the σ,σ^* absorption band of the silicon skeleton. The lifetimes are of the order of picoseconds for both the sharp and the broad bands. The intensity of the broad emission monotonically decreases as the temperature increases from 4.2 K to ~180 K, whereas the intensity of the sharp emission remains nearly constant. From these experiments together with the previous theoretical considerations we conclude that the broad emission band is an emission from the intrapolymer skeleton σ to pendant π^* charge transfer state.

1. Introduction

The photoluminescence of poly(methylphenylsilylene), $(CH_3C_6H_5Si)_n$ (often referred to as methylphenylpolysilane), was first reported by Kagawa et al.[1] The luminescence is composed of two bands: a relatively sharp (fwhm ~500 cm^{-1}) band at 350 nm and a significantly broad (fwhm ~5000 cm^{-1}) and structureless band in the 400–500-nm region. The sharp band in the short-wavelength side is also observed for poly(methylpropylsilylene) and is understood to be the σ^*,σ interband transition delocalized over the silicon skeleton. The broad band in the long-wavelength side, on the other hand, is observed only when phenyl groups are substituted on the silicon skeleton.

Two different mechanisms for this broad luminescence have been proposed. Kagawa et al.[1] ascribed it to an emission from a charge-transfer state between the silicon skeleton and the phenyl pendants. Harrah and Zeigler,[2] on the other hand, claimed that the broad luminescence was due to an impurity generated by photolysis of the polymer.

In the present paper, we try to make a more conclusive assignment of the broad luminescence located in the long-wavelength region. To this end, various spectroscopic measurements were carried out at very low temperatures, under which condition any photodegradation of the polymer is unlikely to take place. As will be discussed in detail below, we conclude that the broad luminescence is due to a charge-transfer state between the skeleton σ orbital delocalized over the whole silicon chain and the pendant π^* orbital.

For the sake of brevity, the two types of emission bands will hereafter be referred to simply as "the sharp band" and "the broad band".

2. Experimental Section

Poly(methylphenylsilylene) was prepared by polymerization of methylphenyldichlorosilane using sodium metal in boiling toluene in a manner described by West.[3] The crude polymer thus prepared was purified first by washing with methanol and then by the freeze dry method. The molecular weight distribution measured by gel permeation chromatography is shown in Figure 1. The maximum is found at a molecular weight of 1.2×10^5. The synthesized polymer was further fractionated into different molecular weights by a Shodex GPC-A-804 gel permeation chromatograph. All the processes of synthesis, purification, and measurements were carried out under yellow light so that any photochemical degradation of the polymer is inhibited.

The emission was investigated for both *p*-dioxane solutions (concentration of 1.6×10^{-3} M with respect to Si atom) and films. Dioxane used as a solvent was purified by fractional distillation. The films were prepared by the spin coating on a SiO_2 substrate. The molecular weight of the polymer used in the film was 0.7×10^5.

The emission spectra were obtained with a $^3/_4$-m Spex 1702 monochromator equipped with a Hamamatsu R928 photomultiplier tube. The excitation was carried out by light from a 500-W Xe lamp passed through a 30-cm Nalumi double monochromator. The excitation spectra were corrected for the wavelength dependence of the monochromator and the light distribution of the Xe lamp by means of a Rhodamine 6G quantum counter.

In the case of the decay measurements, the excitation was carried out by a Molectron UV-400 nitrogen laser. The decay signal was digitized by an Iwatsu DM-900 digital memory, and the digital data were transferred to a microcomputer for signal averaging.

The spectra were measured at various temperatures between 4.2 and ~180 K. The temperatures above the liquid helium temperature were controlled by an Osaka Sanso Cryomini-O closed cycle cryogenic system.

3. Results

(a) Emission and Excitation Spectra. Figure 2 shows the emission spectra observed for a dioxane solution and for a spin coated film at 4.2 K. The spectra are qualitatively similar to the spectrum observed by Kagawa et al.[1] for a coated film at 77 K. That is, the spectrum is composed of the sharp band in the short-wavelength side and the broad band in the long-wavelength side.

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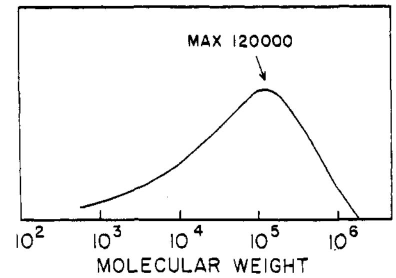

Figure 1. Molecular weight distribution of synthesized $(CH_3C_6H_5Si)_n$ in chloroform measured by gel permeation chromatography.

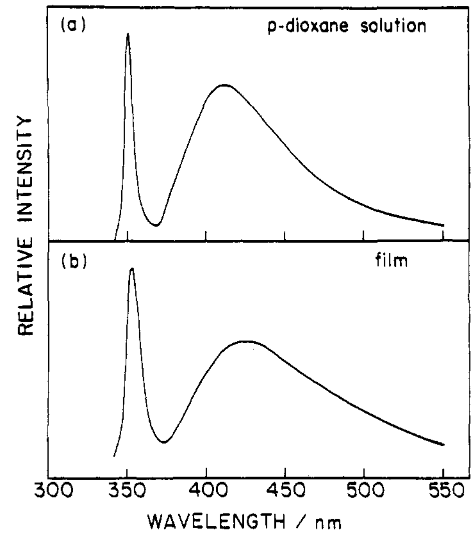

Figure 2. Emission spectra of $(CH_3C_6H_5Si)_n$ measured at 4.2 K for (a) a *p*-dioxane solution and (b) a film, excitation wavelength being 300 nm.

Even though the spectrum from the solid is a little wider as compared with the spectrum from the solution, the two spectra are quite similar. Because of the similarity of the spectra, one might argue that the solution spectrum is, in fact, the spectrum from the solid that is segregated from solution at low temperature. This possibility is, however, unlikely in view of the fact that the solution spectrum is almost independent of concentration (vide infra). We may thus assume that the spectrum shown in Figure 2a really represents the solution spectrum.

The excitation spectra observed at 4.2 K for the dioxane solution and for the film are shown in parts a and b of Figure 3, respectively. The solid and dotted curves refer to the sharp and the broad emission bands, respectively. The absorption spectra observed at room temperature for a dioxane solution are shown in Figure 3c for comparison. The two peaks located at ~280 and ~345 nm mainly correspond, respectively, to the σ,σ^* transition of the silicon skeleton and the π,π^* transition of the phenyl pendants.[1] The most remarkable observation is that the excitation spectra sensitively vary with the monitor wavelength. As is clearly seen in Figure 3a,b, the broad band emission is more enhanced by the π,π^* excitation of the pendants as compared with the σ,σ^* excitation of the skeleton.

Efforts have been devoted to examine if there exists, in the long-wavelength tail of the absorption spectrum, any additional band which could be assigned as the reverse absorption to the broad emission band. With a concentrated solution, very weak absorption was indeed observed at the tail of the first absorption band. The spectrum is also shown in Figure 3c.

(b) Concentration Dependence. The effect of concentration on the spectral distribution was examined at 77 K for dioxane solutions of the following concentrations: 8.3×10^{-3}, 1.4×10^{-3}, 2.3×10^{-4}, and 3.8×10^{-5} M with respect to Si atom. For the solution with the highest concentration, the relative intensity of the sharp band with respect to the broad band is about 10% smaller, probably due to the self-absorption process. For the solution with the lowest concentration, the emission intensity is too small to make quantitative measurements. The two solutions of intermediate concentrations have exactly identical spectral distribution. (For example: the sharp/broad intensity ratio of 100/8, the sharp band at 351 nm, the broad band at approximately 420 nm, etc.) We thus conclude that the main feature of the spectrum is independent of the polymer concentration.

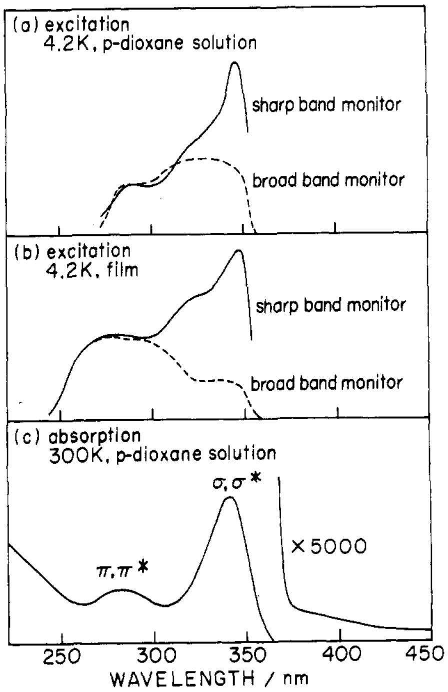

Figure 3. Excitation spectra of $(CH_3C_6H_5Si)_n$ measured at 4.2 K for (a) a *p*-dioxane solution and (b) a film, monitored at the sharp band (solid curve) and the broad band (dotted curve). (c) Absorption spectrum of $(CH_3C_6H_5Si)_n$ observed at 300 K for a *p*-dioxane solution (5.6×10^{-5} M with respect to Si atom). The spectrum in the longer wavelength tail is measured for a concentrated (0.1 M) benzene solution.

(c) Molecular Weight Dependence. In view of the fact that the synthesized polymer has a quite wide molecular weight distribution, as is shown in Figure 1, one might query if the broad spectral feature is due to the wide molecular weight distribution. In order to examine this query, the sample polymers were separated into seven parts, molecular weights of the individual parts being as follows: 2×10^6–1.3×10^5, 1.3×10^5–6.5×10^4, 1.8×10^4–9×10^3, 9×10^3–4×10^3, 4×10^3–1.5×10^3. All seven parts were found to have identical spectral distributions. We thus conclude that the emission spectrum is almost independent of molecular weight, at least in the range 1500–2×10^6, and that the broad spectral feature is not due to the wide molecular weight distribution.

(d) Effect of Photodegradation of the Polymer. When the measurement of the emission spectrum is made at temperatures above ~180 K, the intensity of the sharp band tends to be decreased with time. This experimental finding appears to be due to photodegradation of the polymer. The effect of photodegradation was examined in more detail in the following manner. A dioxane solution was irradiated by light from a xenon lamp for a certain period at room temperature, and then the solution was

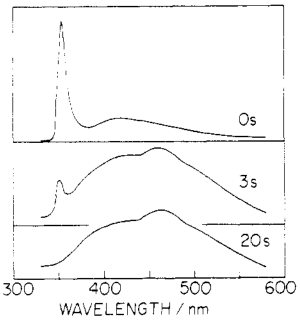

Figure 4. Effect of photodegradation of $(CH_3C_6H_5Si)_n$ on the 77 K emission spectrum. The dioxane solution of $(CH_3C_6H_5Si)_n$ is irradiated for various time intervals (0, 3, and 20 s), and then the solution is cooled to 77 K, and the emission spectrum is measured.

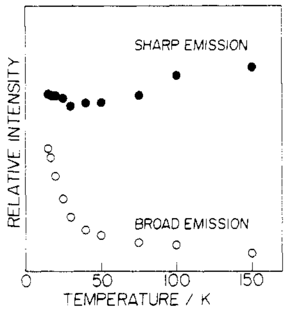

Figure 5. Temperature dependence of the emission spectrum of $(CH_3C_6H_5Si)_n$, excitation being carried out at 300 nm.

cooled to 77 K, and the emission spectrum was observed. A quite significant effect was observed, as is shown in Figure 4. With the irradiation of light for 3 s, the intensity of the sharp band decreases remarkably, and a new broad band emerges at around 465 nm. With irradiation for 20 s, another new broad band appears at around 380 nm. Both of the newly developed bands are different from the broad band originally present.

It should be emphasized that the photodegradation discussed here takes place only at a temperature higher than ~180 K. It is quite certain that, at 77 K and below, no photochemical degradation of the polymer takes place.

(e) Temperature Dependence on the Emission Intensity. Figure 5 shows the temperature dependence of the emission intensity of the sharp and the broad bands. As the temperature increases, the intensity of the broad band decreases monotonically, whereas the intensity of the sharp band remains nearly constant. The temperature dependence could be examined only up to ~150 K; above ~180 K irradiation induces, as is discussed above, diminution of the sharp band and the appearance of new broad bands due to photodegradation of the polymer.

(f) Decay Measurements. Effort has been devoted to determine the decay rate constants associated with the two types of emission at 4.2 K by exciting with a nitrogen laser of ~10-ns pulse width. For the sharp band, the time profile of the emission was found exactly identical with the laser pulse. We can only conclude therefore that the lifetime is shorter than 10 ns. This statement is almost true for the broad band, too; the time profile was nearly identical with that of the laser pulse. The closer examination of the tail of the decay reveals, however, that there exists a very slight contribution of a long-lived (~5-ms) component. The intensity of this component is so small that we will not be bothered with this long-lived component in the present paper. (Our preliminary picosecond measurements indicate that the lifetime is approximately 50 ps for the sharp bands and ~1 ns for the broad band. Details will be reported in the near future.[4])

4. Discussion

As is discussed above, the sharp emission band in the short-wavelength side is an emission from the σ,σ^* excited state of the skeleton delocalized over the whole silicon chain, whereas the origin of the broad emission band in the long-wavelength side is controversial. In the following, we try to identify the origin of the broad band.

It is, for the first time, important to assure that the observed band is not due to an impurity. First of all, we have ascertained that the chemicals used for the polymerization (i.e., methylphenyldichlorosilane, toluene, and metallic sodium) do not exhibit any emission. That is, no emissive impurities were present in the starting materials. It is thus clear that the emission is due to some kind of reaction product. During the purification processes, any raw materials and a product of low molecular weight are certainly removed. We thus ought to conclude that the observed emission is at least from the polymer product. The fact that the excitation spectrum monitored for the broad band nearly coincides with the absorption spectrum of poly(methylphenylsilylene) almost excludes a possibility of an impurity emission, for it is almost impossible to conceive of a reaction starting from the same materials and ending up a different polymer, having an absorption spectrum identical with the polymer in question.

In addition to these, we wish to emphasize that the polymer sample does not contain any trace of a photoproduct. As is stated above, during the whole processes of synthesis, purification, and measurements, the polymer is exclusively avoided from the exposure to UV light at temperatures above 180 K. In repeated spectroscopic measurements carried out at temperatures between 4.2 and 180 K, neither diminution of the sharp band nor the increase of the broad band could be detected; all the results were quite reproducible.

Thus, we conclude that the broad emission is not due to any sort of impurity but is intrinsic to the polymer. In the following, therefore, we try to examine what kind of excited state of the polymer is responsible for the broad emission.

As is discussed above, the broad emission band lies at longer wavelength than the σ,σ^* emission of the skeleton. Also, the lowest energy π,π^* excited state of the phenyl pendant lies at higher energy than the lowest σ,σ^* excited state of the skeleton. It is thus quite clear that the excited state responsible for the broad band is located at lower energy than any of the lowest σ,σ^* states of the skeleton and π,π^* states of the pendants. From this viewpoint, only the following three mechanisms can be conceived as plausible candidates for the source of the broad band. These are (a) excimer emission, (b) phosphorescence emission, (c) emission from interpolymer or intrapolymer charge-transfer state between the skeleton and the pendants. In what follows, we shall examine which of these mechanisms is the most reasonable in view of the experimental evidence discussed above.

(a) Examination of the Possibility of the Excimer Emission. The broad and structureless emission located at the long-wavelength region is reminiscent of the intrapolymer excimer fluorescence associated with the aromatic moieties substituted to the polymer chain.[5-14] However, this mechanism is unlikely because of the following grounds.

First, the broad band is located at too long a wavelength to be considered as the excimer fluorescence. Usually,[15] the peak of the excimer fluorescence is separated from the 0,0 band of the monomer fluorescence by ~6000 cm^{-1}. In the present case, however, the peak of the broad band is separated from the monomer fluorescence of benzene (not observed for the polymer) by $\sim$13 000 cm^{-1}. Further, the broad band in question differs significantly from the known[16] excimer fluorescence of benzene whose peak is located at $\sim$320 nm. Even though the configuration of the excimer, if it existed in the present polymer, may as well be different from that found in the carbon-based polymers or for solutions, energy separation twice as large appears unreasonable.

Second, the temperature dependence of the emission intensity observed for the broad band differs from that usually found for excimer fluorescence. Generally, the temperature dependence of the intensity of excimer fluorescence is characterized by an inverted "U"-shape behavior.[13] That is, as the temperature increases, the intensity first increases, reaching the maximum at a certain temperature, and then decreases. This is due to the competition between the thermally assisted side-chain motion and excimer dissociation process; the former predominates at lower temperature region and the latter predominates at higher temperature region. In contrast to this general behavior, the intensity of the broad band in question decreases monotonically with temperature as is shown in Figure 5. Thus, the possibility of the intrapolymer excimer fluorescence is completely ruled out. The interpolymer excimer fluorescence is more unlikely in view of the fact that the intensity of the broad band is almost independent of the polymer concentration (vide supra).

(b) Examination of the Possibility of the Phosphorescence Emission. The emission located at the longer wavelength region might be due to the phosphorescence emission. In fact, the phosphorescence from the locally excited triplet state of an aromatic substituent has been observed for some silicon-based polymers.[10] This mechanism is also unlikely because of the following grounds.

The observed emission is certainly not the phosphorescence from $^3(\pi,\pi^*)$ localized on the phenyl pendant; it differs completely from the phosphorescence of benzene both in its spectral location and lifetime. The location and spectral properties of $^3(\sigma,\sigma^*)$ of the skeleton are unknown at present. However, the possibility of the $^3(\sigma,\sigma^*)$ emission can be discarded in view of the very short lifetime ($\leq$10 ns) observed for the broad band. Even though the silicon atom tends to decrease the phosphorescence lifetime due to the heavy atom effect,[10,17] the observed lifetime is too short to interpret it as the lifetime of the triplet excited state. The possibility of an emission from either $^3(\pi,\pi^*)$ of the pendant or $^3(\sigma,\sigma^*)$ of the skeleton is thus ruled out.

The location and properties of the triplet state of the excimer are also unknown, but again, the broad band cannot be ascribed to the triplet excimer in view of the reasons discussed in (a) and also of the lifetime.

(c) Examination of the Possibility of a Charge-Transfer Fluorescence. Since both the excimer emission and the phosphorescence emission have been denied as the origin of the broad band in the above discussion, only the plausible mechanism which is left uneliminated appears to be some kind of charge-transfer emission between the skeleton and pendants. In view of the experimental finding that the intensity of the broad band is independent of the concentration of the polymer, we conclude that any *inter*polymer charge-transfer states do not play a role. Thus, what should be examined is only the *intra*polymer charge-transfer state between a σ orbital of the skeleton delocalized over the whole Si chain and a π orbital of the pendant localized on the phenyl substituents. In fact, the broad emission band observed here for the polymer is analogous, in both the spectral location and the spectral shape, to the charge-transfer fluorescence spectrum observed for phenyldisilane and its analogues.[17]

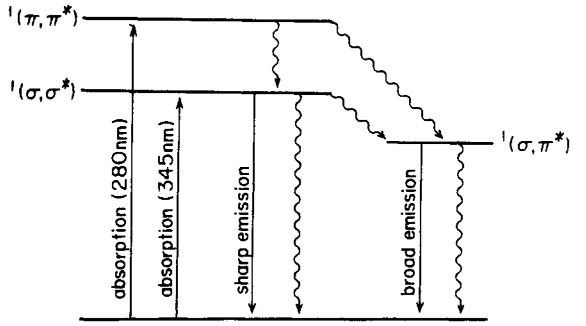

Figure 6. Schematic representation of the energy levels and the radiative and nonradiative processes. The solid arrows indicate the emissions, and the wavy arrows indicate nonradiative processes.

The nature of the charge-transfer state needs to be discussed. Previously, Kagawa et al.[1] presumed that the broad band was due to an emission from the π,σ^* state, that is, the radiative recombination of the electron in the Si–Si antibonding σ^* conduction band and the hole in the bonding π orbital originating from the π orbitals of the phenyl pendants. This assignment was based on their preliminary band structure calculations, in which the π bonding orbital was located in between the σ^* conduction band and the σ valence band. More refined calculations carried out by Takeda et al.,[18] however, reveal that the π bonding orbital is located well below the σ valence band. Namely, according to the refined calculations, a hole in the π bonding orbital cannot be created by the σ,σ^* excitation, and therefore, the π,σ^* state should lie at considerably higher energy than even the π,π^* state. In the following, we shall examine if the experimental findings discussed above can be reasonably interpreted within the framework of the emission from the intrapolymer σ,π^* skeleton to pendant charge-transfer state. Various radiative and radiationless deactivation processes relevant to this mechanism are schematically shown in Figure 6.

The mechanism shown in Figure 6 accounts well for the experimental finding that either σ,σ^* or π,π^* excitation gives rise to both the sharp and the broad emissions. The fact that the excitation spectra for the sharp band and the broad band are mutually different indicates that there exists direct radiationless deactivation process from the π,π^* state to the σ,π^* state. Due to this radiationless process, the σ,π^* emission is more enhanced by the π,π^* excitation as compared with the σ,σ^* excitation.

Existence of dual fluorescence might at first suggest that the broad emission is a so-called TICT (twisted intramolecular charge transfer) fluorescence.[19] The TICT fluorescence, however, is unlikely. First of all, in the present polymer, rotation of a phenyl group around the Si–C bond does not necessarily induce the complete charge transfer and the subsequent energy stabilization. Second, the fact that the broad emission is observed at as low a temperature as 4.2 K contradicts what is expected for the TICT fluorescence.[20] Third, the monotonic intensity decrease with the increase of temperature as is shown in Figure 5 is different from the temperature dependence expected for the TICT fluorescence.[20]

We thus ought to conclude that the observed broad band is not the TICT fluorescence. In this case, then, we need to have an explanation why the intrapolymer radiationless deactivation from the σ,σ^* excited state to the σ,π^* charge-transfer state is slow to such an extent that it can compete with the σ,σ^* fluorescence. It should be either that the σ,σ^* fluorescence is extremely fast or that the above radiationless process is extremely slow. In order to examine this, we try to determine the radiative rate constant for the σ,σ^* fluorescence from the absorptivity of the reverse transition. In evaluating the ϵ value from the observed absorptivity, we assume that the molecular weight of the polymer is uniformly 1.2×10^5 (peak value in Figure 1). With this assumption, ϵ at the peak of the absorption (~340 nm) is determined as 8.7×10^6 cm^{-1} M^{-1}. The radiative rate constant for the reverse emission is then determined as 5×10^{10} s^{-1}. It has thus been clarified that the σ,σ^* fluorescence is a significantly fast process; it can easily compete with the radiationless transition to the σ,π^* state. Large absorptivity found for the transition to the σ,σ^* state and hence the high emissivity of the σ,σ^* emission is understood also theoretically in view of the large density of state at the bottom of the σ^* conduction band as is seen in Takeda et al.[18]

The source of the temperature dependence observed for the broad band is not quite understood at this moment. A decrease of fluorescence or phosphorescence intensity at higher temperature is quite commonly observed for many organic molecules and is usually interpreted in terms of the existence of a fast decaying electronic or vibronic state. However, such a significant temperature dependence of the intensity at such a low-temperature region is not so common. The discussion of this subject therefore has to be postponed until the experiments on the temperature dependence of the lifetime are completed.

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Fluorescence Probes for Evaluating Chain Solvation in Network Polymers. An Analysis of the Solvatochromic Shift of the Dansyl Probe in Macroporous Styrene–Divinylbenzene and Styrene–Diisopropenylbenzene Copolymers

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ABSTRACT: The wavelength of the fluorescence emission of dansyl probe **1** in pure organic solvent is red shifted as the solvent polarity, hydrogen bond donor ability, and hydrogen bond acceptor ability are increased. A variety of network polymers "doped" with **1** have been synthesized. An analysis of the solvatochromic shift of the fluorescence emission of these materials when imbibed in solvents has been found to correlate with the facility with which solvents penetrate the gel or continuous phase of these materials. The analysis is accomplished by comparisons of the fluorescence emission of **1** in dry polymer with that of the solvent-imbibed polymer. As expected, solvent penetrability decreases with increasing cross-linking density and is significantly influenced by the morphology of the material. The gel phase of macroporous resins can be significantly more penetrable than nonporous "beads" of comparable cross-linking. The nature of the porogen is found to exert a profound effect on the penetrability of macroporous materials. Support for the interpretation of the solvatochromic results is obtained from hydrolysis studies of bisketal templates that were incorporated into the matrix of the polymers by copolymerization. The hydrolysis yields in both tetrahydrofuran and methanol increase with increased solvent penetrability as revealed by the solvatochromic shift. The hydrolysis results in tetrahydrofuran are also paralleled by swelling studies; thus, a large volume increase in THF is paralleled by a high hydrolysis yield (THF/H_2O). The swelling ratio in methanol, however, does not correlate with hydrolysis yield. The probe technique permits survey of a variety of complex materials of widely different morphology.

Introduction

The facility with which solvents may penetrate the gel phase of a network polymer is an issue of fundamental importance,[1,2] and diagnositics have been employed to evaluate this phenomenon.[3] Network polymers of complex morphology, such as macroporous resins,[4] pose particularly

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