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Studies on Hybrid Organic/Inorganic Nanocomposite Gels Using Photoluminescence Techniques

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Summary. Transparent nanocomposite gels made of hybrid organic/inorganic polymers, synthesized through the sol-gel method, composed of poly-(ethylene oxide) or poly-(propylene oxide) chains, and grafted on silica through urea bridges, have been studied by steady-state and time-resolved photoluminescence techniques. These nanocomposite materials consist of two distinguished subphases, an organic and an inorganic one. The volume fraction of the organic (polyether) subphase is larger than that of the inorganic (silica) subphase, and it increases with increasing polyether chain size. The condensation of the silica subphase provides luminescent entities emitting light by electron-hole recombination on delocalized states associated with the active chemical species of the urea bridges. Materials with smaller polyether chains are more luminescent than such with longer polyether chains. Divalent or trivalent cations introduced into these materials enhance the luminescence intensity by solubilization close to the silica cluster surface and thus by decreasing surface defects and the ensuing quenching mechanism.

Keywords. Fluorescence spectroscopy; Organic/inorganic gels; Ureasils.

Introduction

The study of organic/inorganic nanocomposite gels prepared by the sol-gel method comprising poly-(ethylene oxide) (*PEO*) or poly-(propylene oxide) (*PPO*) chains grafted on silica nanoparticles by means of urea bridges (Ureasils) is an area that has recently attracted a lot of interest. Ureasils have been used as ion-conducting solid state electrolytes [1, 2] and as hosts of luminescent lanthanides [3, 4], at the same time making interesting luminescent phosphors by themselves [3–5]. In addition, the organic content of the gels offers a parameter of mechanical flexibility as well as a possibility of index of refraction variation and control. Characterization of the structure and study of some dynamic aspects of these materials has been achieved by different techniques [6, 7]. They can be thought in general as

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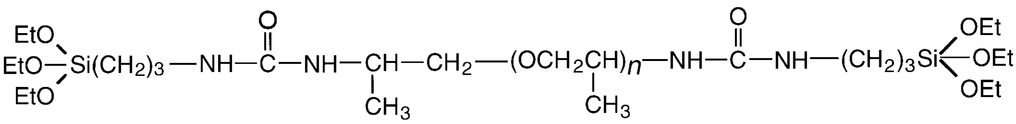
nanocomposite blends of organic and inorganic domains which form interpenetrating networks [6]. The small size of the domains and the large differences in their dynamic behavior necessitate a large range of spectroscopic techniques for their proper characterization [6]. One technique particularly suited for nanoheterogeneous systems is steady-state and time-resolved analysis of fluorescence quenching between hosted probes. An application of this technique to the study of nanocomposite blends of SiO_2 with poly-(ethylene glycol) oligomers has been previously published [8]. In the present work we apply the same technique to obtain information on the structure of ureasils. By exploiting the intrinsic luminescence of these hybrid materials we show how certain parameters such as polyether chain length and the presence of cations can affect luminescence intensity.

Results and Discussion

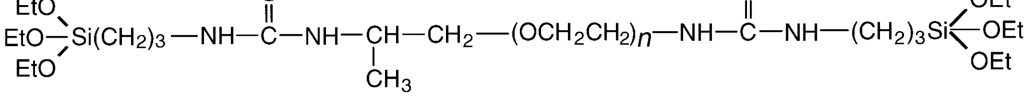
The materials investigated in the present work are shown in Fig. 1. Pyrene is an aromatic hydrocarbon which has been systematically used as a fluorescent probe of nanoheterogeneous systems, particularly in colloidal solutions such as micelles. It has a relatively long decay time (a few hundreds of nanoseconds), forms excimers in a dynamic process, and possesses a rich vibronic structure in its fluorescent spectrum that reflects the polarity of the molecular environment. Monomer or excimer fluorescence can be favoured by choosing the appropriate pyrene concentration. Pyrene was incorporated in the nanocomposite gels at various concentrations by solubilization in the precursor sols. Figure 2 shows the fluorescence spectrum of pyrene monomers in two characteristic ureasils, *PPO* 230 and *PPO* 2000. The relative intensity of the first vibronic peak is lower in the case of *PPO* 2000 and even lower in *PPO* 4000. It is known that the first vibronic transition in the pyrene fluorescence spectrum is a symmetry-forbidden transition [9]. In polar

PPO 4000/2000/230 (*n* ~ 68/33/3)



$$(EtO)_3Si(CH_2)_3{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_2{-}(OCH_2\underset{CH_3}{\underset{|}{CH}})_n{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_3Si(OEt)_3$$

PEO 1900/800/500 (*n* ~ 43/18/12)



$$(EtO)_3Si(CH_2)_3{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_2{-}(OCH_2CH_2)_n{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_3Si(OEt)_3$$

Fig. 1. Chemical structures of the poly-(propylene oxide) (*PPO*) and poly-(ethylene oxide) (*PEO*) containing precursors

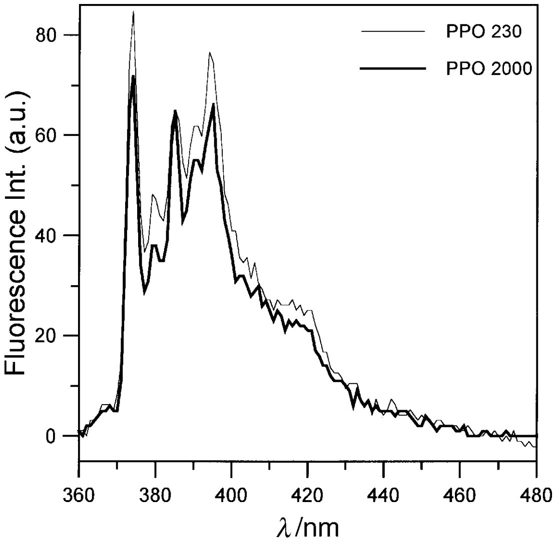


Fig. 2. Fluorescence of pyrene monomers solubilized in gels formed of precursors with two different chain lengths

environments, symmetry is perturbed by interaction with neighboring polar species. Then the symmetry rule is weakened, and the first transition becomes more intense. The opposite is true for non-polar environments. It has been found that longer poly-(propylene oxide) chains provide materials with less polar environment than shorter chains. More details on studies of ureasils based on pyrene fluorescence vibronic structure are given in Ref. [10]. It is concluded that in order to obtain an environment of varying polarity, the materials should organize themselves in a manner that would provide two separate subphases: (1) the polar silica subphase obtained by inorganic polymerization and (2) the polyether subphase. The existence of the two subphases is then unambiguously reflected in the vibronic structure of pyrene monomer fluorescence.

When the pyrene concentration in the original sol was increased to $10^{-3}\,M$, excimers were formed by interaction between an unexcited and an excited pyrene molecule. Excimers are readily formed in fluid environments. They are also found in the present nanocomposite gels due to the existence of the organic subphase that facilitates molecular diffusion and interaction. Of course, interaction between an excited and an unexcited pyrene molecule can also take place in aggregated form. However, analysis of pyrene decay profiles of both excimer and monomer emission (cf. Ref. [8]) has shown that in the present ureasils interaction occurs by a dynamic process, and pure excimers are formed. No aggregates have been detected by inspection of absorption spectra either. The analysis of the fluorescence decay profiles of pyrene monomers in the presence of excimers has been carried out by fitting a model of stretched exponentials [8] according to Eq. (1).

$$I(t) = I_0 \exp(-t/\tau_o)\exp(-C_1(t/\tau_o)^f + C_2(t/\tau_o)^{2f}) \quad (0 < f < 1) \qquad (1)$$

More details on analyses with this model can be found in Ref. [8] and references therein. The value of f is a measure of the restrictions imposed by the environment on the probe. The f values found with the three *PPO* ureasils were close to the percolation threshold ($f = 0.67$ [11]), whereas slightly smaller values were obtained with *PEO* ureasils. By assuming that pyrene is solubilized in the organic subphase, pyrene fluorescence probing of ureasils points to limited silica domains dispersed in an organic subphase that constitutes most of the material's volume. The silica domains are, however, interconnected; otherwise, the material could not form a solid gel. Gelation is thus due to limited but interconnected silica domains.

On top of the silica nanoparticles there is a high concentration of C=O and NH groups provided by the urea bridges. These groups seem to be responsible for the ability of ureasils to produce photoluminescence. Precursors of ureasils, *i.e.* the original materials before hydrolysis and condensation, as the those shown in Fig. 1, are also luminescent. Precursors are expected to aggregate, *i.e.* to attain some kind of molecular organization, owing to the difference of polarity between the silicate end groups and the polyether chains as well as to hydrogen bridging between C=O and NH groups of different precursor molecules. The only way to explain precursor luminescence, which is not present at high dilution [10], is to assume that the organization of the monomers creates a situation where a silicate-rich domain is distinguished from a polyether-rich domain. Silicate-rich domains should be covered by a layer of the urea groups. It is interesting to note that a mature precursor fluid and a nanocomposite gel emit luminescence of a similar spectral structure (Fig. 3). The only common characteristic between these materials is the presence of C=O and NH groups on the surface of silicon containing domains. We conclude that surface states provided by these groups are responsible for luminescence emission by delocalized electron-hole recombination processes.

The emission of ureasils decreases with increasing polyether chain length for both *PPO* and *PEO* (Table 1). In addition to the decrease of luminescence intensity due to decreasing concentration of emitting species in a more bulky organic

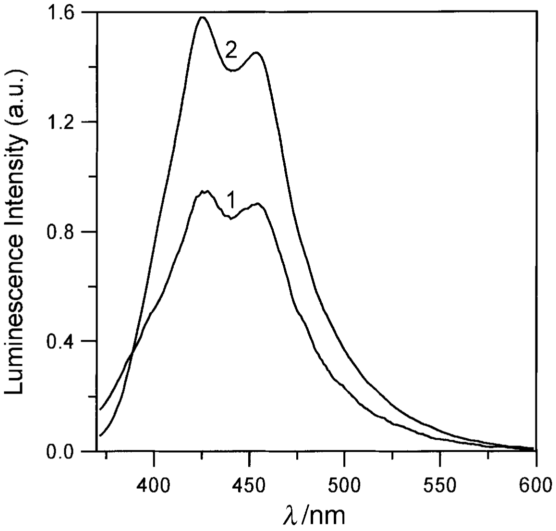


Fig. 3. Luminescence spectra of a mature precursor fluid *PEO* 800 (1) and of the ensuing *PEO* 800 gel after sol-gel polymerization (2)

Table 1. Variation of luminescence intensity of dry gels with respect to polyether chain length; excitation wavelength: 360 nm

Material	Luminescence intensity (a.u.)
PPO 230	1140
PPO 2000	387
PPO 4000	208
PEO 500	897
PEO 800	698
PEO 1900	341

subphase, increasing polyether chain length obviously increases defects on emitting centers, thus decreasing luminescence efficiency by extensive quenching. The most intensively luminescent ureasils are those prepared from small polyether chains.

Finally, ureasils can be enriched with divalent or trivalent cationic species. Luminescent lanthanide ions enhance their luminescence intensity when incorporated in such matrices owing to the creation of an environment protective against quenching processes due to complexation with polyether chains [3, 4]. However, in ureasils cations are expected to form complexes also with the urea groups. It has been found that cations increase intrinsic ureasil luminescence by such camplexation, apparently by curing surface defects. This property is shown by both divalent and trivalent ions, no matter whether they are luminescent or not by themselves. For example, Cd^{2+} increases *PEO* 800 luminescence three-fold by incorporating cations at a ratio of one Cd^{2+} ion per 170 urea groups. More details on these results can be obtained from Ref. [12].

In conclusion, ureasils can be described as fine dispersions of silica domains in an organic polyether solvent, altogether forming a nanocomposite gel. The dispersed domain luminesces by delocalized electron-hole recombination involving states provided by active urea groups. Luminescence intensity is high (*i*) when the ether chains are short and (*ii*) in the presence of small amounts of divalent or trivalent cations. Ureasils are efficient hosts of lanthanide emitters since they provide a protective environment by complexation with polyether chains.

Experimental

The synthesis of the precursors has been described elsewhere [10]. The sol-gel polymerization was performed using the following procedure: 4.5 g of precursor were mixed with 15 cm^3 of MeOH. After stirring for 5 min, 0.5 cm^3 of 0.1 *M* HCl was added, and the mixture was stirred for 30 more min. After further stirring the fluids were put in uncovered square PMMA cuvettes and left to dry in air for one week. Dopants were introduced after previous solubilization in methanol.

Measurements were performed at 20°C. Absorption measurements were carried out with a Cary 1E spectrophotometer. Steady-state fluorescence measurements were made with a home-assembled spectrofluorometer using Oriel parts. Time-resolved fluorescence decay profiles were recorded with the single-photon counting technique using a home-made nanosecond flash lamp and ORTEC electronics.

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