Transparent Polysilsesquioxane Films Obtained from Bridged Ureasil Precursors: Tunable Photoluminescence Emission in the Visible Region and Filtering of UV-Radiation

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Bridged ureasil precursors were synthesized by the reaction of either ethylenediamine (1 mol) or *m*-xylylenediamine (1 mol) with isocyanatepropyltriethoxysilane (2 mol). Transparent polysilsesquioxane films were obtained by the hydrolytic condensation of the pure precursors or their co-condensation in a 50:50 molar ratio. Films based on pure ureasil precursors showed a blue photoluminescent emission band assigned to the photoinduced proton-transfer among H-bonded urea groups and the subsequent radiative recombination of ionized groups. Films synthesized by the co-condensation of both precursors exhibited a significant red-shift of their absorption, excitation, and emission spectra, associated to de-localization of H-bonds, and a high absorption of UV-radiation.

Introduction

Organic–inorganic hybrid materials obtained by the sol–gel method represent a promising family of materials for technological applications due to the possibility of mixing organic and inorganic components at the nanometer scale, the ability of tailoring their final properties through the composition and conditions of the synthesis and the processing versatility.[1–4] Besides, they can fulfill the series of requirements imposed for functional applications of advanced materials such as thermal, humidity, UV-light resistance, and hydrophobicity.[5–9]

Bridged silsesquioxanes are a particular class of organic–inorganic hybrid materials synthesized by the hydrolytic condensation of typical precursors like $(RO)_3-Si-R'-Si-(RO)_3$, where RO represents an alkoxy group and R' is an organic group. The hydrolysis and condensation of the terminal alkoxysilane groups produces Si−O−Si bonds that generate inorganic clusters covalently bonded by organic bridges (R') forming a crosslinked structure.[10–21] When the organic bridge contains groups that can be associated through Van der Waals forces, H-bonds, π–π interactions, etc., self-assembled domains of organic bridges are generated.

Ureasils are bridged silsesquioxanes where R' contains one or more urea groups. Typical precursors of ureasils are obtained by the reaction of isocyanatepropyltriethoxysilane (IPTES, 2 mol) with a diamine (1 mol). The hydrolysis

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and condensation of this precursor generates an ureasil containing two urea groups in the organic bridge. The presence of urea groups promotes the self-assembly of organic bridges by strong H-bonds. The size of the resulting organic clusters depends on the competition between the rate of inorganic polymerization and the rate of self-assembly of organic bridges,[22] associated with the chemical structure and length of the organic bridge.[23]

A distinctive characteristic of ureasils is their intrinsic photoluminescence arising from electron–hole recombinations in the inorganic domains (purplish-blue band) and photoinduced proton-transfer between urea groups convoluted with the emission from the inorganic clusters (blue band).[22–31] The location of both bands remains constant at low excitation wavelengths but a red-shift of both bands and a decrease in intensity is typically observed by increasing the excitation wavelength above a threshold value.[28] For practical applications it is interesting to analyze the possibility of tuning the emission in different wavelength regions covering the whole visible spectrum. This may be accomplished by: (i) doping the diureasil with an appropriate dye enabling energy transfer from the blue band to the dye (antenna effect); (ii) red-shift the original blue band by delocalizing the H-bonds in the self-assembled structure of organic bridges. As an example of the first possibility, we recently reported that doping a diureasil with safranin enabled an efficient energy transfer between the blue-band emission and the dye absorption leading to a strong red-emission.[32] Red-shift of the original blue band was produced by varying the conditions of the synthesis to affect the competition between the rate of inorganic polycondensation and the rate of self-assembly of organic bridges.[22]

The aim of this manuscript is to discuss an original way to produce a red-shift of the original blue band emission employing the co-condensation of two different ureasil precursors. The main hypothesis was that using two different precursors with organic bridges that could be placed at random in the self-assembled organic domains would lead to a partial de-localization of H-bonds and a corresponding red-shift of the emission spectrum. For this purpose we employed two precursors based on the reaction of IPTES (2 mol) with either ethylenediamine (EDA, 1 mol) or *m*-xylylenediamine (XDA, 1 mol). Figure 1 shows the structure of the resulting precursors. The length of the organic bridge of the precursor synthesized with XDA was higher than the one synthesized with EDA by the length of an aromatic ring. However, as we will analyze in the Results and Discussion Section, both types of organic bridges could be randomly intercalated in the self-assembled structures.
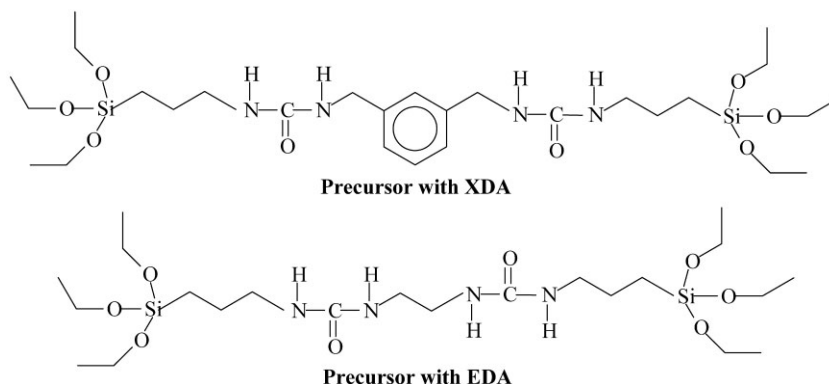

Figure 1. Chemical structures of the precursors synthesized by the reaction of IPTES (2 mol) with XDA (1 mol) or with EDA (1 mol).

Absorbance and photoluminescence spectra of films synthesized with pure precursors or a 50:50 molar ratio of both precursors, are reported and analyzed.

Experimental Part

Synthesis of the Ureasil Precursors

Stoichiometric amounts of IPTES (Fluka, >95% purity) and either XDA (Aldrich) or EDA (Sintorgan, analytical grade) were dissolved in isopropanol (i-PrOH, Sintorgan, analytical grade). Typically, 100 mL of the i-PrOH solution were employed with a 0.30 M concentration of IPTES and a 0.15 M concentration of XDA or EDA. Due to the high rate of reaction, solutions of the diamine and IPTES in i-PrOH were first prepared at room temperature. Then, the solution containing the diamine was added slowly to the solution containing IPTES. Due to the exothermic character of the reaction a small temperature increase was observed. The resulting solution was kept 2 h at room temperature with continuous stirring and the completion of reaction was confirmed by the disappearance of the strong absorption peak of the isocyanate group at $2\,272\,cm^{-1}$ in Fourier-transformed infrared (FTIR) spectra.

Synthesis of Polysilsesquioxane Films

Polysilsesquioxane films were synthesized as follows. A 0.1 M i-PrOH solution of a pure ureasil precursor or a 50:50 molar blend of both precursors was prepared. The hydrolysis and polycondensation was performed at room temperature (about 18 °C), adding formic acid (FA) and water (W) in the following molar ratios: FA/Si = 0.1 and W/Si = 3. Solutions (15 mL) were cast in polyacetal recipients of 5 cm diameter with a glass cover that enabled the control of the solvent evaporation rate. After about 4 weeks the resulting self-standing transparent films could be easily detached from the plastic recipient. The resulting polysilsesquioxane films will be designed as: P-XDA, P-EDA, and P-XDA/EDA.

Characterization Techniques

X-ray diffraction (XRD) was performed with a Philips PW1710 diffractometer using the Cu Kα radiation, in the 2θ range comprised
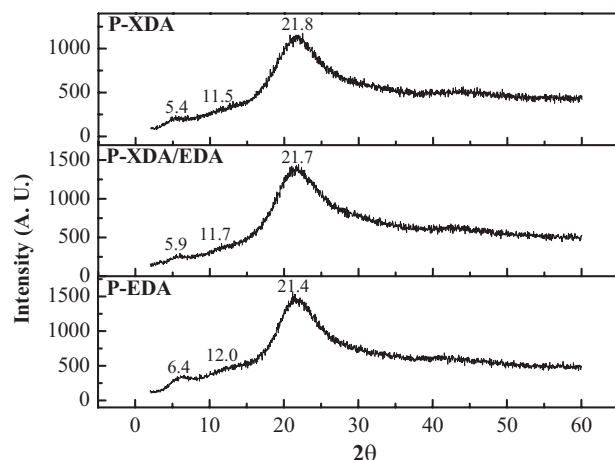
Figure 2. X-ray diffractograms of the different polysilsesquioxane films.

between 2 and 60°. FTIR spectra were recorded with a Nicolet 6700 device (Thermo Scientific) in the absorbance mode, in the range 400–4 000 cm^{-1} with a resolution of 4 cm^{-1}. Spectra were obtained by ATR employing 32 scans. Absorption spectra were obtained using a diode-array UV-vis spectrophotometer (Hewlett–Packard 8453). Emission spectra in steady state were obtained at room temperature with a Spex Fluoromax spectrofluorometer. A solid sample holder placed at 45° was employed; all measurements were performed in a front surface geometry at room temperature employing samples with the same thickness.

Results and Discussion

Characterization of the Polysilsesquioxane Films

All the synthesized polysilsesquioxane films were self-standing and transparent with a thickness close to 400 μm. While films synthesized from pure precursors (P-XDA and P-EDA) were colorless, films synthesized with the blend of precursors (P-XDA/EDA) were yellow. This evidenced the fact that the absorption spectra were modified by using the blend of ureasil precursors.

X-ray diffractograms of the polysilsesquioxane films are shown in Figure 2. The films were amorphous and exhibited

two broad peaks: the main one at 2θ close to 21.6° and a small one at 2θ close to 6° with a shoulder at about twice this value. The location of these peaks and the corresponding values of the scattering vectors ($q = 4\pi \sin \theta/\lambda$, where $\lambda = 0.1542$ nm for the Cu Kα radiation), and characteristic lengths ($d = 2\pi/q$), are shown in Table 1. The main peak associated with $d = 0.41$ nm is characteristic of the packing distance of alkyl chains.[20,33] In our case, this characteristic length can be associated to the distance between organic bridges in self-assembled structures. The important conclusion is that the co-condensation of two different precursors with similar lengths of organic bridges did not alter the packing density of the self-assembled structures. The small peak located at low angles corresponds to a characteristic distance equal to the length of the organic bridge. The presence of a shoulder at about $2q$, within experimental error, can be assigned to a lamellar structure with a short-range order, composed of alternating layers of siliceous domains and organic bridges. Again, the co-condensation of the two precursors did not alter the main structure of the bridged silsesquioxane. As expected, the length of the organic bridge is shorter for P-EDA and larger for P-XDA; the film prepared from the blend of both precursors shows an intermediate value. A schematic representation of the structure of ureasils is presented in Figure 3.
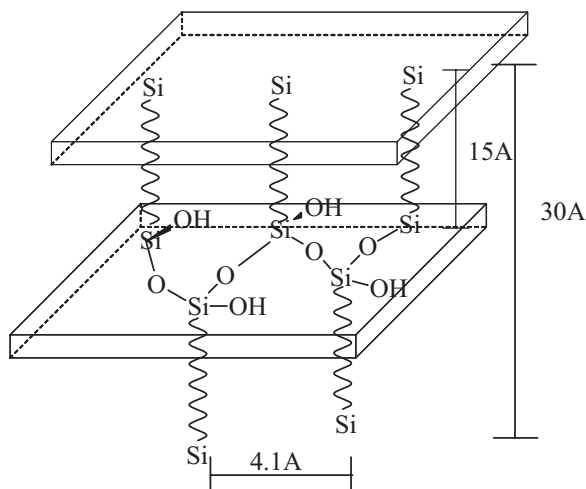
FTIR spectra of the polysilsesquioxane films in the region of the amide I and amide II bands are shown in Figure 4. A deconvolution of these bands was performed employing 4 Gaussian peaks and the Origin 7.0 software. The location and partial contribution to the intensity of the amide I band of the three peaks found for the different polysilsesquioxane films, is shown in Table 2. According to the literature, the peak located at about 1 625 cm^{-1} can be assigned to C=O groups H-bonded with a very high strength (designed as localized H-bonds in Table 2), the peak close to 1 648 cm^{-1} corresponds to high-strength H-bonded C=O groups, and the peak located in the region 1 670–1 690 cm^{-1} is assigned to low-strength H-bonded C=O groups.[34] It is observed that P-XDA had the largest fraction of localized H-bonds and the lowest fraction of low-strength H-bonds. This is possible the consequence of the symmetric orientation of

Table 1. Location of the peaks, scattering vectors (q) and characteristic lengths (d) in XRD spectra of the polysilsesquioxane films.

Film	Peak	q	d	Peak	q	Peak	q	d
	°2θ	nm^{-1}	nm	°2θ	nm^{-1}	°2θ	nm^{-1}	nm
P-XDA	5.355	3.81	1.65	11.500	8.16	21.790	15.40	0.41
P-XDA/EDA	5.895	4.19	1.50	11.670	8.29	21.690	15.34	0.41
P-EDA	6.405	4.55	1.38	12.015	8.53	21.405	15.14	0.41

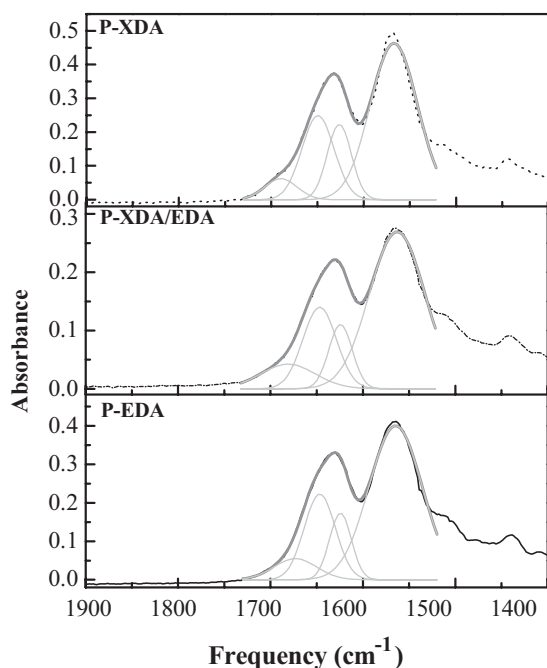Figure 3. Schematic representation of the structure of polysilses-quioxane films.

Table 2. Location and partial contribution to the intensity of the amide I band of the three peaks found for the different poly-silsesquioxane films in FTIR spectra.

Film	Localized H-bonds		High-strength H-bonds		Low-strength H-bonds	
	ν cm^{-1}	%	ν cm^{-1}	%	ν cm^{-1}	%
P-XDA	1 626	34.9	1 649	52.2	1 690	12.9
P-XDA/EDA	1 624	27.0	1 647	49.2	1 681	23.8
P-EDA	1 624	29.2	1 647	52.8	1 673	18.0

UV-Vis Absorption Spectra of Polysilsesquioxane Films

The UV-vis absorption spectra of the polysilsesquioxane films are shown in Figure 5 (due to the high absorbance of the 400 μm films only tails of the absorption peaks were recorded). The film synthesized using a blend of both precursors showed a significant shift of the absorption band to the visible region, a fact that explains its yellow color. As discussed in Introduction Section, the photoinduced proton transfer between H-bonded groups is responsible for bands appearing in absorption, excitation, and emission spectra. The disorder introduced in the self-assembly of organic bridges by the random placing of two different precursors produced an increase in the fraction of low-strength H-bonds (as proved by FTIR spectra), and, consequently, a decrease in the average energy absorbed in the photo-induced proton transfer. This explains the shift of the absorption band of P-XDA/EDA to the visible region.

The tail of the absorption band of P-XDA/EDA exhibits a sharp drop at about 420 nm (Figure 5). This film might find applications as a transparent coating for UV-sensitive
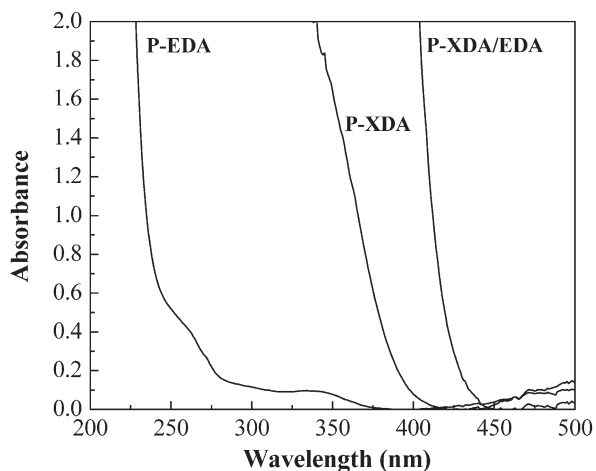

Figure 4. FTIR spectra of the polysilsesquioxane films in the region of the amide I and amide II bands.

urea groups in the P-XDA bridge and their asymmetric orientation in the P-EDA bridge (Figure 1). The film synthesized using the blend of both precursors exhibited the lowest fraction of localized H-bonds and the largest fraction of low-strength H-bonds. This is the consequence of the disorder introduced by the random placing of two different precursors in the self-assembled organic structure.

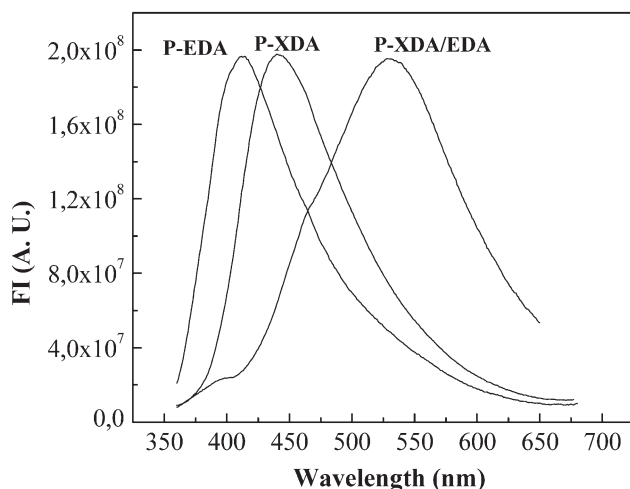Figure 5. UV-vis absorption spectra of polysilsequioxane films.

Figure 6. Normalized emission spectra of the polysilsesquioxane films (excitation wavelength = 350 nm).

materials, replacing coatings containing dispersions of ZnO or TiO_2 nanoparticles that absorb UV light up to the proximity of the visible spectrum and are transparent at visible wavelengths.[35]

Photoluminescence Spectra of the Polysilsesquioxane Films

The emission spectra of the different polysilsesquioxane films (normalized to their maximum of emission) are shown in Figure 6 for an excitation wavelength of 350 nm.

The film synthesized using a blend of both precursors exhibited a significant red-shift of the emission band explained by the de-localization of H-bonds between organic bridges.

Figure 7–9 show excitation and emission spectra of P-EDA, P-XDA, and P-XDA/EDA, respectively. For P-EDA there are at least two main contributions to the photoluminescence in the visible region (Figure 7). The most intense emission band has a maximum at about 410 nm and its location does not depend significantly on the excitation wavelength. The maximum intensity was observed for an excitation wavelength close to 350 nm. This band results from a radiation process characterized by a constant energy gap between excited and ground states. We ascribed this emission to the photoinduced proton transfer with subsequent radiative recombination in geometrically well-defined urea–urea hydrogen bonds (corresponding to the localized and high

strength H-bonds of Table 2). Overlapped with this band there is a less-intense broad band with a maximum that is red-shifted when increasing the excitation wavelength. This second band contributes to the emission up to wavelengths of about 500–550 nm. This band is assigned to proton transfer and subsequent radiative recombination in de-localized H-bonds exhibiting a distribution of energies. The presence of (at least) two sources of emission is clearly observed in the excitation spectrum for the emission at 500 nm. The spectrum exhibits two maxima: one at 350 nm corresponding to the residual emission at 500 nm of the main emission band (maximum at 410 nm), and the other one at about 400 nm assigned to the excitation of the less-intense emission band.

A similar behavior is observed for the emission of the P-XDA film (Figure 8). Now, the most intense emission band has a maximum at about 460 nm and its location shows a slight red-shift when increasing the excitation wavelength. The maximum intensity was observed for an excitation wavelength close to 400 nm. This localized band is assigned to the photoinduced proton transfer between geometrically well-defined H-bonded urea groups. In this ureasil the broad and less-intense emission band, assigned to proton transfer in de-localized H-bonds, contributes less to the overall emission than in the case of P-EDA. Its presence is evidenced as a shoulder in the excitation spectrum for an emission at 550 nm. The smaller contribution of the de-localized emission band in the case of P-XDA with respect to P-EDA, may be correlated with the smaller fraction of low-strength H-bonds in P-XDA with respect to P-EDA, as was observed by FTIR (Table 2).

For P-XDA/EDA the most intense emission band has a maximum in the range 530–550 nm, when varying the excitation wavelength from 300 to 500 nm (Figure 9). The maximum intensity was observed for an excitation wavelength of about 450 nm. A shoulder located at about
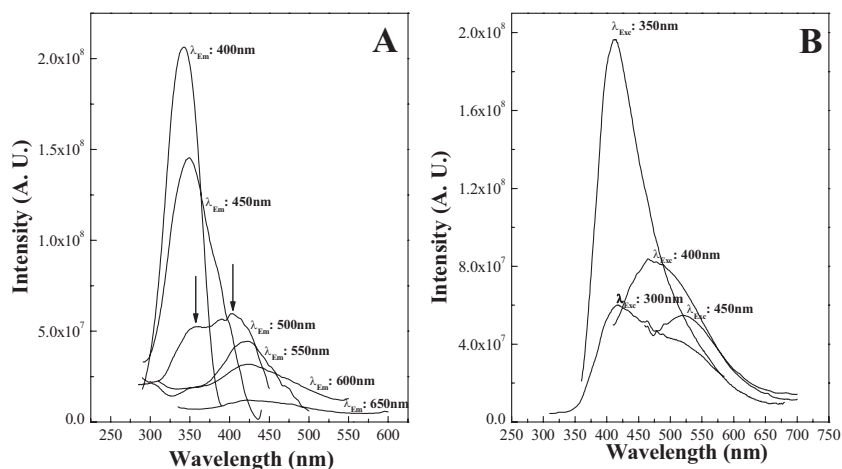

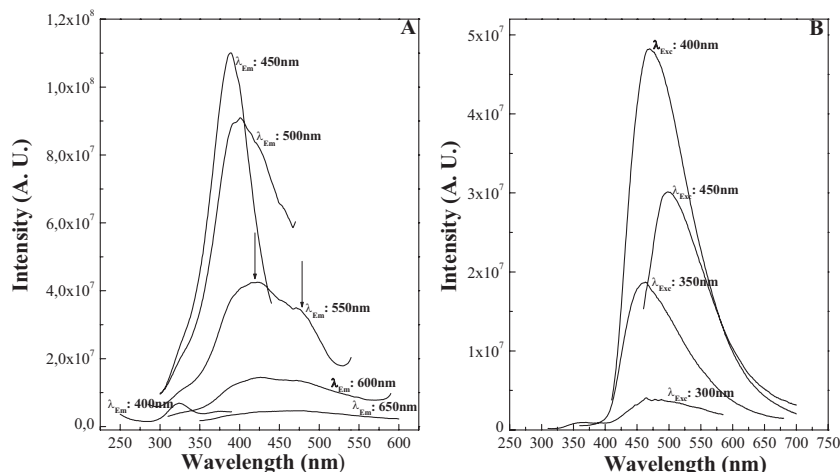*Figure 7.* Excitation (A) and emission (B) spectra of P-EDA.

Figure 8. Excitation (A) and emission (B) spectra of P-XDA.
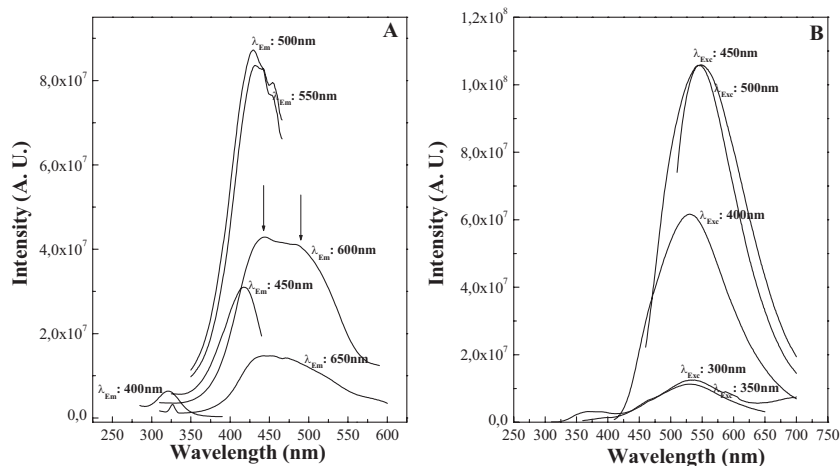

Figure 9. Excitation (A) and emission (B) spectra of P-XDA/EDA.

450 nm is observed in the emission band obtained for an excitation wavelength of 400 nm. The presence of two emission bands is evidenced in the excitation spectrum for an emission of 600 nm. This band exhibits two maxima: one at about 440 nm assigned to the excitation of the localized band; the other one at about 480 nm assigned to the excitation of the de-localized emission band. Most of the contribution to the overall emission arises from the de-localized band in agreement with the FTIR spectra (Table 2), showing that the sample P-XDA/EDA contains the highest amount of low-strength H-bonds. The very small band observed in the excitation spectrum for an emission wavelength of 400 nm is assigned to the emission from inorganic domains.[34]

The main contribution to the photoluminescence of the pure polysilsesquioxane films arises from a localized

emission band that is slightly red-shifted when increasing the excitation wavelength. A less-intense de-localized emission band makes an additional contribution in the region of high wavelengths. The localized emission band is assigned to the photoinduced proton transfer and subsequent radiative recombination in H-bonded urea–urea groups of high strength. The location of this band depends on the structure of the organic bridge. For P-EDA the maximum emission is close to 410 nm; for P-XDA the maximum emission was observed at about 460 nm.

A deconvolution of emission bands for an excitation length of 350 nm is presented in Figure 10 for the three different polysilsesquioxanes. The contribution of bands arising from localized and de-localized H-bonds is significant for the polysilsesquioxane films obtained from pure precursors. However, for the film synthesized using the blend of precursors most of the contribution to the emission band arises from the de-localized H-bonds. Therefore, for polysilsesquioxane films synthesized with blends of both precursors the most important contribution to the luminescence is the emission arising from proton transfer and subsequent radiative recombination in de-localized H-bonds exhibiting a distribution of energies. De-localization is the result of variations in chain conformations produced when assembling organic bridges of different chemical structure. This reduces the average energy necessary for proton transfer in H-bonded urea groups, a fact that produces a red-shift in both absorption and emission spectra.

Conclusion

Polysilsesquioxane films synthesized by the co-condensation of two different ureasil precursors with similar lengths of organic bridges showed a significant red-shift of their absorption, excitation, and emission spectra when compared to films synthesized from a single ureasil precursor. Based on the mechanism proposed in the literature associating the emission in the visible region to radiative recombination following photoinduced proton transfer in H-bonded urea groups,[28,30] we explained the observed
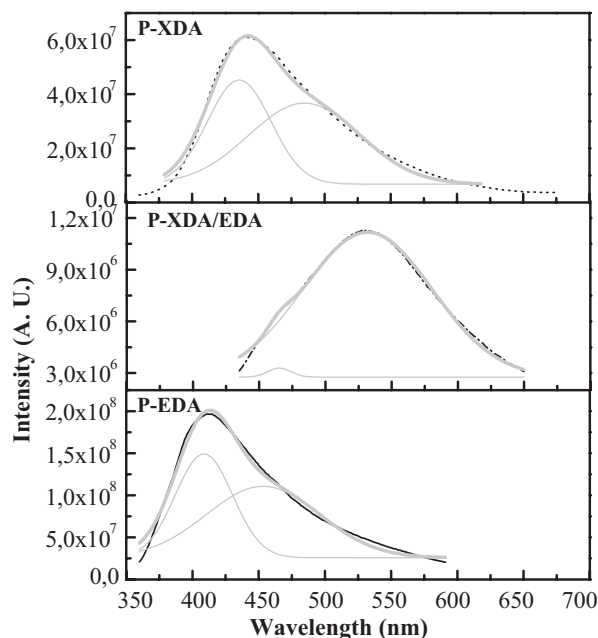
Figure 10. Deconvolution of the emission spectra of polysilsesquioxane films obtained employing an excitation wavelength of 350 nm.

behavior to de-localization of H-bonds produced by variations in the conformation of the organic bridges of the two different precursors when they are assembled at random between siliceous domains. An interesting property of P-XDA/EDA films is the high absorption of UV-radiation while keeping transparency in the visible region. Coatings based on these materials might find applications as UV-filters.

 [1] H. D. Gesser, P. C. Goswami, *Chem. Rev.* **1989**, *89*, 765.
 [2] C. Sanchez, G. J. de. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chem. Mater.* **2001**, *13*, 3061.
 [3] S. Zaioncs, K. Dahmouche, B. G. Soares, *Macromol. Mater. Eng.* **2010**, *295*, 243.
 [4] D. L. Versace, A. Chemtob, C. Croutxé-Barghorn, S. Rigolet, *Macromol. Mater. Eng.* **2010**, *295*, 355.
 [5] A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897.
 [6] L. D. Carlos, R. A. Sá Ferreira, V. de Zea Bermudez, S. J. L. Ribeiro, *Adv. Mater.* **2009**, *21*, 509.
 [7] S. Hu, D. Yang, Y. Xu, D. Wu, Y. Sun, *Mater. Chem. Phys.* **2009**, *114*, 868.
 [8] H. Deka, N. Karak, *Prog. Org. Coat.* **2009**, *66*, 192.
 [9] M. Sangermano, R. Bongiovanni, M. Longhin, G. Rizza, C. M. Kausch, Y. Kim, R. R. Thomas, *Macromol. Mater. Eng.* **2009**, *294*, 525.
[10] K. J. Shea, D. A. Loy, O. W. Webster, *Chem. Mater.* **1989**, *1*, 512.
[11] K. J. Shea, D. A. O. W. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700.
[12] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, *Chem. Mater.* **1992**, *4*, 1217.
[13] D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431.
[14] G. Cerveau, R. J. P. Corriu, *Coord. Chem. Rev.* **1998**, *178-180*, 1051.
[15] R. J. P. Corriu, *Polyhedron* **1998**, *17*, 925.
[16] R. J. P. Corriu, *Angew. Chem., Int. Ed.* **2000**, *39*, 1376.
[17] K. J. Shea, D. A. Loy, *Acc. Chem. Res.* **2001**, *34*, 707.
[18] K. J. Shea, D. A. Loy, *MRS Bull.* **2001**, *26*, 368.
[19] K. J. Shea, D. A. Loy, *Chem. Mater.* **2001**, *13*, 3306.
[20] H. E. Romeo, M. A. Fanovich, R. J. J. Williams, L. Matějka, J. Pleštil, J. Brus, *Macromolecules* **2007**, *40*, 1435.
[21] H. E. Romeo, M. A. Fanovich, R. J. J. Williams, L. Matějka, J. Pleštil, J. Brus, *Macromol. Chem. Phys.* **2007**, *208*, 1202.
[22] D. P. Fasce, R. J. J. Williams, L. Matějka, J. Pleštil, J. Brus, B. Serrano, J. C. Cabanelas, J. Baselga, *Macromolecules* **2006**, *39*, 3794.
[23] M. L. Gómez, D. P. Fasce, R. J. J. Williams, C. M. Previtali, L. Matějka, J. Pleštil, J. Brus, *Macromol. Chem. Phys.* **2008**, *209*, 634.
[24] L. D. Carlos, V. de Zea Bermudez, R. A. Sá Ferreira, L. Marques, M. Assunção, *Chem. Mater.* **1999**, *11*, 581.
[25] L. D. Carlos, R. A. Sá Ferreira, I. Orion, V. de Zea Bermudez, J. J. Rocha, *J. Lumin.* **2000**, *87-89*, 702.
[26] L. D. Carlos, L. R. A. Sá Ferreira, V. de Zea Bermudez, S. I. L. Ribeiro, *Adv. Funct. Mater.* **2001**, *11*, 111.
[27] T. Brankova, V. Bekiari, P. Lianos, *Chem. Mater.* **2003**, *15*, 1855.
[28] L. D. Carlos, R. A. Sá Ferreira, R. N. Pereira, M. Assunção, V. de Zea Bermudez, *J. Phys. Chem. B* **2004**, *108*, 14924.
[29] L. Fu, R. A. Sá Ferreira, N. J. O. Silva, L. D. Carlos, V. de Zea Bermudez, J. Rocha, *Chem. Mater.* **2004**, *16*, 1507.
[30] S. S. Nobre, P. P. Lima, L. Mafra, R. A. Sá Ferreira, R. O. Freire, L. Fu, U. Pischel, V. de Zea Bermudez, O. L. Malta, L. D. Carlos, *J. Phys. Chem. C* **2007**, *111*, 3275.
[31] L. Fu, R. A. Sá Ferreira, M. Fernandes, S. C. Nunes, V. de Zea Bermudez, G. Hungerford, J. Rocha, L. D. Carlos, *Opt. Mater.* **2008**, *30*, 1058.
[32] M. L. Gómez, D. P. Fasce, R. J. J. Williams, H. A. Montejano, C. M. Previtali, *J. Polym. Sci., B: Polym. Phys.* **2008**, *46*, 289.
[33] A. Shimojima, K. Kuroda, *Chem. Rec.* **2006**, *6*, 53.
[34] S. C. Nunes, V. de Zea Bermudez, J. Cybinska, R. A. Sá Ferreira, J. Legendziewicz, L. D. Carlos, M. M. Silva, M. J. Smith, D. Ostrovskii, J. Rocha, *J. Mater. Chem.* **2005**, *15*, 3876.
[35] W. Caseri, *Chem. Eng. Commun.* **2009**, *196*, 549.