

Luminescence of heat-treated silicon-based polymers: promising materials for LED applications

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Abstract A new strategy to obtain transparent, thermally stable, and formable photoluminescent materials for LED applications is presented. Starting from commercially available silicon-based polymers, luminescence properties are developed by means of simple heat treatment. Solid polymethylsilsesquioxane MK (Wacker-Besil[®]PMS MK) and liquid poly(ureamethylvinyl)silazane Ceraset (Kion Ceraset[®] PUVMS) were thermally treated between 200 and 700 °C for 2 h under Ar atmosphere. Photoluminescence properties were observed in all the samples. The structural rearrangements during thermal annealing were effective in order to red-shift the emission spectra of the untreated polymers to the visible range. The formation of dangling bonds and carbon sp², associated with the annealing procedure and confirmed by means of Electron Paramagnetic Resonance (EPR) spectroscopy and solid state Magic Angle Spinning NMR (MAS-NMR) contribute to the red-shift of the photoluminescence emissions of the polymers. After heat treatment at low temperatures (200, 300, and 400 °C), both the polymers show fluorescence in the UV

range. While the polysiloxane reveals white luminescence after annealing at 500 and 600 °C, the polysilazane heat-treated at 500 °C exhibits emission in the blue-green range and is transparent. At higher temperatures the presence of free carbon counteracts the luminescence properties.

Introduction

In recent years, a considerable amount of academic and industrial research has been directed to the development of photoluminescent materials for Light Emitting Diodes (LEDs).

However, inorganic LEDs based on a semiconductor chip coated with a light converting material, such as powdered phosphor suspended in a resin, still encounter problems of sedimentation during the processing [1, 2]. Moreover, the resin matrix is subjected to photodegradation under UV light and to damage under moisture and at high temperatures [3, 4]. Rare earth doped glasses avoid these problems by offering homogeneity, transparency, and excellent stability against temperature, radiation, and moisture, but they require high processing temperatures for molding (approximately 1,250–1,500 °C) [5, 6]. Other promising luminescent materials are π and σ conjugated polymers. They exhibit advantages such as formability and flexibility, but they are sensitive to air, moisture, high-energy radiation, and high temperatures [7–10].

Thus, the development of light converting materials insensitive to air and moisture and easy to process is still a challenging research task. In the present article, we propose a new approach to obtain transparent, thermally stable, and formable photoluminescent materials starting from cheap, non toxic, and commercially available polyorganosiloxanes

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and polyorganosilazanes by means of simple heat treatment. In fact, we observed that the structural rearrangements and temperature induced formation of radicals during the annealing of the Si-based polymers resulted in luminescence properties in the visible range.

The thermal stability of Si-based polymers was shown in numerous reports [7, 11, 12]. Low temperature heat treatment (200–500 °C) is effective in crosslinking the inorganic polymer to obtain a transparent solid material which can attain the shape of a mold [13–15]. Disadvantages such as sedimentation, non homogeneity, and high temperature molding can be overcome by using traditional organosilicon polymer processing techniques. Therefore, silicon-based polymers combine the temperature stability of glasses with the excellent formability of organic polymers and may provide attractive alternative materials for the production of LED [9, 10].

Experimental

The commercially available polymethylsilsesquioxane Wacker-Belsil[®] PMS MK (Wacker Chemie AG, Munich, Germany), $(\text{CH}_3\text{-SiO}_{3/2})_x$, and the poly(ureamethylvinyl)silazane (PUMVS, CerasetTM) (KiON Corp., Clariant, USA), $(\text{-NH}(\text{CH}_3)\text{SiH-})_{0.77}(\text{-NRC=O})_{0.01}(\text{NH}(\text{HC=CH}_2)\text{SiCH}_3)_{0.22}$, were used as precursors [15].

The samples were prepared by thermolysis of the polymer (2 g) in a quartz crucible placed in a quartz tube under a steady flow of argon (50 mL/min) in a horizontal Al_2O_3 tube furnace (Gero-Öfen, Typ 40-300/7 85), at a heating rate of 50 °C/h from room temperature to the target temperature, followed by 2 h dwelling time and free cooling to room temperature.

The fluorescence measurements were recorded in air on Cary Eclipse, Varian Spectrophotometer using a Xenon lamp as the excitation source, sensitive across the whole wavelength range. The samples were measured in powder form in 1 mm precision cells made of Quartz Suprasil[®], 100-QS, Hellma[®]. The fluorescence spectra were deconvoluted using a Gaussian fit in MathWorks (Matlab), Inc. software. The fluorescence intensity was calculated as an integral of the emission spectrum (excitation wavelength see Table 1).

The X-band (9.5 GHz) continuous wave EPR measurements were performed using an ESP 300E spectrometer (Bruker) equipped with a rectangular TE_{112} resonator. The magnetic field was read with a NMR gauss meter (ER 035 M, Bruker). All spectra were recorded at 15 K with an Oxford cryostat. Additionally, a standard field marker (polycrystalline DPPH with $g = 2.0036$) was used for the calibration of the resonance magnetic field values and for the determination of the exact g -factor of the samples. The

Table 1 Excitation and emission wavelengths used to obtain fluorescence spectra for polymethylsilsesquioxane MK and poly(ureamethylvinyl)silazane Ceraset samples

Sample	Excitation wavelength (nm)	Emission wavelength (nm)
MK polymer	225	336
MK 200 °C	225	336
MK 300 °C	225	336
MK 400 °C	230	336
MK 500 °C	306	434
MK 600 °C	306	434
MK 700 °C	350	565
Ceraset 200 °C	247	319
Ceraset 300 °C	247	319
Ceraset 400 °C	304	350
Ceraset 500 °C	350	442
Ceraset 600 °C	424	543

They correspond to the maximum emission and excitation peaks

EPR spectra were best fitted with a superposition of one or two Lorentzian absorption lines in MathWorks, Inc. software.

Solid state Magic Angle Spinning NMR (MAS-NMR) as well as Cross Polarization coupled with Magic Angle Spinning (CP MAS-NMR) experiments were recorded with a Bruker AVANCE 300 spectrometer using a 4 mm rotor diameter. ^{29}Si and ^{13}C NMR experiments were measured at frequencies of 59.62 and 75.47 MHz, respectively. Chemical shifts were referred to tetramethylsilane (TMS).

Results and discussion

In the present study, the fluorescence properties of two commercially available silicon-based polymers heat-treated at different temperatures are discussed, namely polymethylsilsesquioxane (Wacker-Belsil[®] PMS MK) and poly(ureamethylvinyl)silazane (PUMVS, CerasetTM, Kion Corporation).

The emission and excitation spectra were recorded for the maximum intensity excitation or emission peaks, respectively (see Table 1). Furthermore, the emission spectra were recorded using 360 nm as excitation wavelength, as required for LEDs applications (see Electronic supplementary material) [16].

The solid polymethylsilsesquioxane MK was heat-treated at 200, 300, 400, 500, 600, and 700 °C for 2 h under Ar atmosphere. Photoluminescence properties were observed for all the samples. Figure 1a shows the emission and excitation spectra of the MK samples according to Table 1.

The MK polymer and the samples heat-treated at low temperatures (200 and 300 °C) show luminescence in the

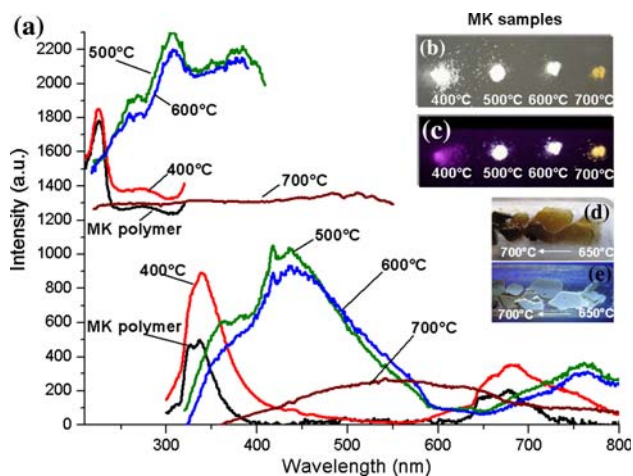


Fig. 1 Fluorescence properties of MK samples heat-treated at different temperatures (labeled). (a) Emission (bottom right) and excitation spectra (top left) of MK obtained with excitation and emission wavelengths according to Table 1. (b) and (c): Photographs representing powdered MK samples under white (b) and UV light (c). (d) and (e): Photographs representing MK annealed with a temperature gradient between 650 and 700 °C, under white (d) and UV light (e)

UV range and are characterized by analogous spectra. Therefore, only the emission and excitation spectra of MK polymer are represented in Fig. 1a.

After heat treatment at 400 °C, the presence of additional red-shifted peaks and an increased contribution of the low energy bands were detected in both the excitation and emission spectra. The samples heat-treated up to 400 °C are transparent and colorless and show fluorescence in the UV range.

After annealing at 500 and 600 °C the MK samples reveal the maximum relative values of fluorescence intensity. The materials are translucent and have a yellow-brown color. Besides the excitation peaks already present in the previous samples, new bands appear at lower energies. Also in the emission spectra new red-shifted peaks are detectable: a part of the spectrum is still in the UV range, but the new peaks in the visible range are responsible for the visible luminescence of the samples.

Following treatment at 700 °C, the luminescence intensity decreases because of the formation of free carbon, as attested from MAS-NMR measurements (Fig. 4), which renders the material dark and opaque [14, 17]. The excitation and emission spectra have the same profile as the previous samples but red-shifted and having lower intensities.

In Fig. 1 powdered MK samples annealed at different temperatures are shown under white (b) and UV light (360 nm) (c). The white luminescence of the samples heat-treated at 500 and 600 °C, is remarkable. A sample of MK annealed with a temperature gradient between 650 and 700 °C, is also shown under white (d) and UV light (e).

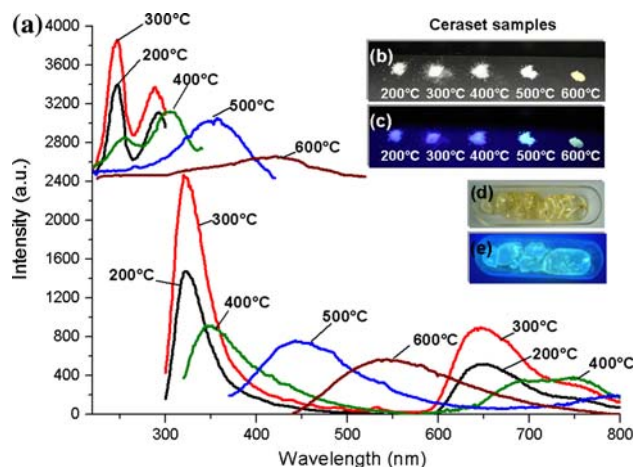


Fig. 2 Fluorescence properties of Ceraset samples heat-treated at different temperatures (labeled). (a) Emission (bottom right) and excitation spectra (top left) of Ceraset obtained with excitation and emission wavelengths according to Table 1. (b) and (c): Photographs representing powdered Ceraset samples under white (b) and UV light (c). (d) and (e): Photographs representing Ceraset annealed at 500 °C under white (d) and UV light (e)

The sample annealed at 650 °C, like the ones heat-treated at 500 and 600 °C, is translucent and colored under white light, while it shows white luminescence and opacity under UV light. Small temperature differences in the annealing have significant effects on the optical properties of the samples.

In the case of the poly(ureamethylvinyl)silazane Ceraset, the liquid precursor was heat-treated at 200, 300, 400, 500, and 600 °C for 2 h under Ar atmosphere. Again, photoluminescence was observed for all the heat-treated samples. Also the liquid precursor shows weak luminescence itself. Figure 2a displays the excitation and emission spectra of the Ceraset annealed at different temperatures according to Table 1.

The samples crosslinked at 200 and 300 °C are transparent and colorless and show luminescence in the UV range. By increasing the temperature from 400 to 600 °C red-shifted excitation and emission ranges are detected compared to the previous samples. After heat treatment at 400 °C the material is still colorless, while at 500 °C it is slightly yellow and remains transparent. The fluorescence intensity decrease at 600 °C, is due to the formation of free carbon, as can be observed in MAS-NMR spectra (Fig. 4) [18–20].

Powdered Ceraset samples annealed at different temperatures are shown in Fig. 2 under white (b) and UV light (c).

Ceraset heat-treated at 500 °C is an interesting material for LED applications. In fact, the whole emission spectrum is in the visible range with excitation maximum around 360 nm. The material is transparent and the processing temperature is significantly decreased compared to the

molding temperature of rare earth doped glasses [5, 6]. In Fig. 2, a bulk sample of Ceraset heat-treated at 500 °C is shown under white (d) and UV light (e). The sample is transparent in both cases, as required for LED applications. However, this research is still at an early stage and further investigations are currently being performed on this material in order to determine its stability under UV irradiation and its suitability for LED applications.

In summary, both the commercially available silicon-based polymers studied here show photoluminescence properties which are developed through heat treatment. The maximum emission intensity in the visible range is obtained for samples annealed at 500–600 °C, decreasing at higher temperatures because of the successive formation of free carbon.

To explain the origin of the luminescence found for the heat-treated Si-based polymers, it is necessary to consider the structural changes and rearrangements associated with the processing temperature. Generally, polysiloxanes and polysilazanes are used as preceramic polymers. The thermolysis of the mentioned polymers at 800–1,200 °C results in polymer derived ceramics (PDCs) [12–15, 17–23]. During heating, bond cleavage and recombination processes occur, i.e., the polymeric structure undergoes a transformation into a three-dimensional solid network structure (ceramic). Therefore, as the temperature increases, dangling bonds (i.e., radicals) are formed [14, 17, 18, 20, 23].

Correlation between luminescence intensity and radical concentration was already observed in sol–gel derived glasses and Si/SiO₂ materials [24–27]. In this study, the presence of dangling bonds was confirmed by means of Electron Paramagnetic Resonance (EPR) spectroscopy.

X-band EPR measurements of MK and Ceraset heat-treated at different temperatures and their numerical simulations were performed. The EPR spectra are characteristic of so-called dangling bonds. All observed species occur in a range of *g*-values of 2.001–2.002, thus the paramagnetic spins are assigned to carbon species, in accordance with the results previously obtained for similar materials [18, 20, 23]. Most of the spectra consist of two overlapping resonances with identical *g*-value but different line width. Accordingly, different hybridization states are distinguished. The sp²-hybridization is characterized by line widths larger than 1 mT and sp³-hybridization by values below 1 mT, due to the different extents of spin delocalization within the “in-plane” dangling bonds [20, 28].

All heat-treated MK samples contain sp³-type carbon dangling bonds, while sp²-hybridized species are observed in the MK polymer only for the samples heat-treated between 500 °C and 700 °C. Consequently, the existence of C=C double bonds is plausible at a temperature as low as 500 °C.

In the case of heat-treated Ceraset samples, sp²-type carbon radicals arise also at low treatment temperatures, due to the presence of vinyl groups in the precursor.

The concentration of carbon dangling bonds was estimated by comparing the measured paramagnetic susceptibility with that of a spin standard of known spin concentration. The radical concentration increases with the heat treatment temperature. An exponential growth can be extrapolated for both MK (a) and Ceraset (b) (Fig. 3).

The heat treatment of the polysiloxane (MK) and polysilazane (Ceraset) at 700 and 600 °C, respectively, results in spin concentrations 3–4 orders of magnitude higher than that of the other samples. Conversely, at these

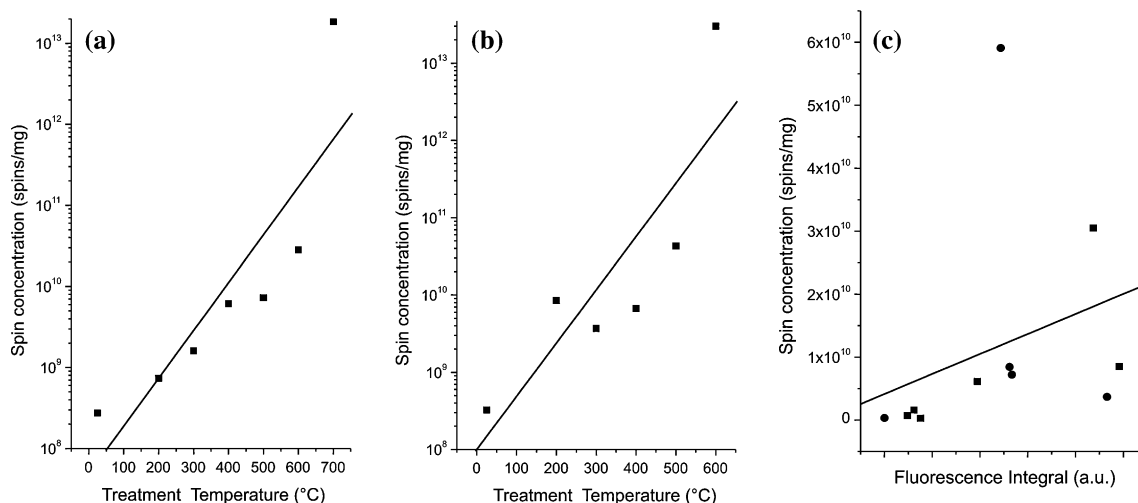


Fig. 3 Dangling bonds concentration. (a) and (b): Exponential growth with temperature of dangling bond centers for MK (a) and Ceraset (b). (c) Correlation of spin concentration and fluorescence intensity (Ceraset: dots, MK: squares)

temperatures lower fluorescence intensities were observed. The reason is the development of free carbon, which negatively influences the fluorescence properties. Therefore, the spin concentrations of such samples cannot be linearly correlated to the fluorescence intensities and are not included in Fig. 3c.

In Fig. 3c the correlation between the dangling-bond concentration and the fluorescence intensity is displayed. The linearity does not fit perfectly. Other mechanisms could also contribute simultaneously to the fluorescence properties, especially at lower temperatures. In fact, by comparing the Ceraset samples heat-treated at 200 and 300 °C, it is clear that radicals concentration does not influence the fluorescence, but the increased crosslinking of the 300 °C sample, as attested from NMR studies (see Fig. 4d), causes higher emission intensity. The reason could be the presence of conjugated bonds in the polymeric chains, hypothesis currently under study. As the crosslinking takes place, the chains rearrange, resulting in stronger emission intensities. At 400 °C and above other mechanisms interfere, which

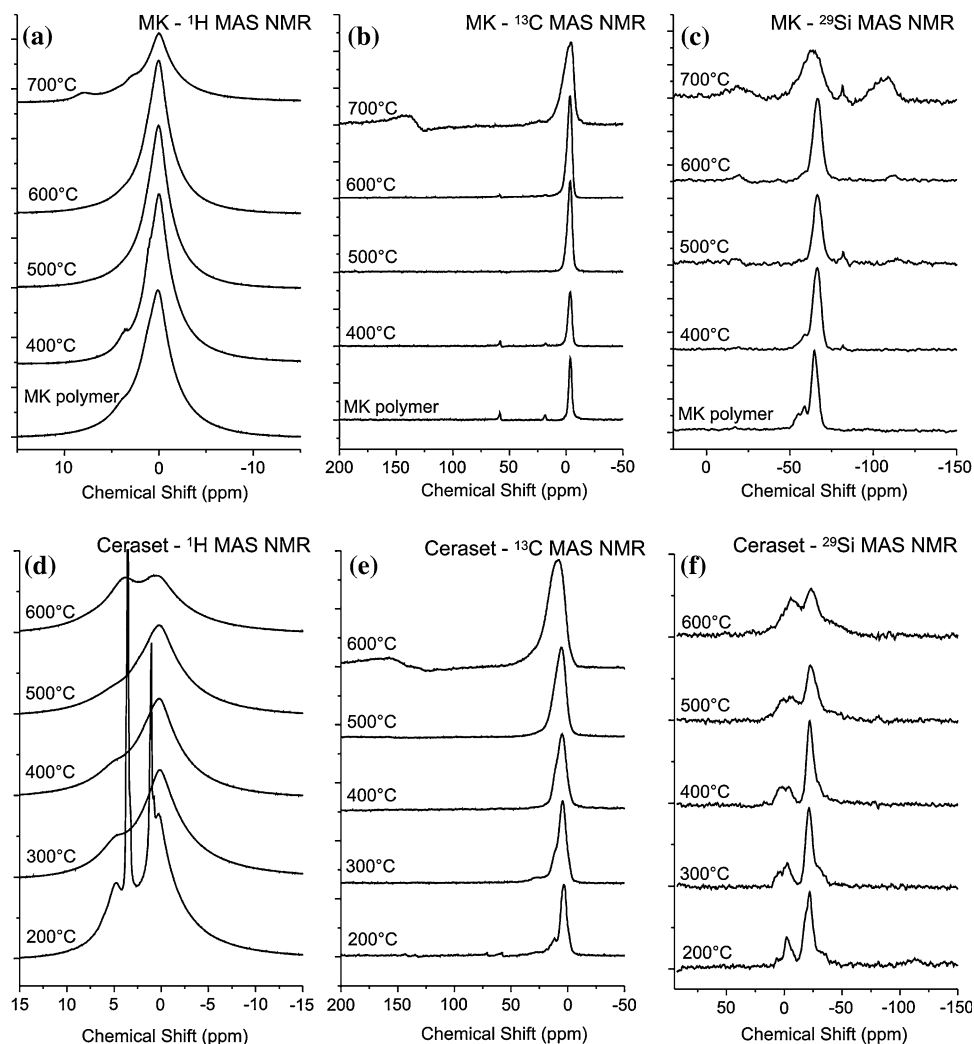
could be the presence of radicals or a higher degree of crosslinking. In fact, in the case of polysilanes, increased branching and crosslinking by means of heat treatment lead to red-shift in emission spectra [29]. This hypothesis is currently under investigation.

By increasing the temperature, red-shifted luminescence spectra were recorded (see Figs. 1a and 2a) [30]. In the same temperature range, carbon double bonds and sp^2 -hybridized carbon radicals form. Thus, as the amount of carbon sp^2 increases with treatment temperature, a red-shift in the emission spectra is detected.

In order to investigate the structural rearrangements of the polymers and to detect the temperature of formation of carbon sp^2 , as observed in EPR investigations, multinuclear MAS-NMR was performed as a complementary structural analysis (Fig. 4).

The thermal transformation of MK by means of NMR is analyzed here for the first time. Free carbon was detected in 1H NMR (protonated carbon sp^2 at 7.95 ppm) and ^{13}C MAS-NMR (141.15 ppm) at 700 °C. The increase of temperature

Fig. 4 Multinuclear MAS-NMR spectra. (a) 1H (b) ^{13}C (c) ^{29}Si MAS-NMR spectra of MK, and (d) 1H (e) ^{13}C (f) ^{29}Si MAS-NMR spectra of Ceraset after annealing at different temperatures as indicated



from 500 to 700 °C results in an enhanced degree of cross-linking of the MK polymer and differently coordinated Si atoms, namely SiO₄, SiO₃C, and SiO₂C₂ identified by ²⁹Si MAS-NMR spectroscopy. The chemical shift value at –81.77 ppm found in the ²⁹Si MAS-NMR spectra of samples annealed between 400 and 700 °C is assigned to the presence of silsesquioxane structural units in the polysiloxane [31].

The thermal transformation of the Ceraset polymer to SiCN ceramic studied by NMR was previously reported [15]. In the present study, we report on complementary NMR results on the thermolysis of Ceraset. In our case, the presence of carbon sp² was observed at 600 °C, a lower temperature than that found in the previous studies [15]. Moreover, at this temperature two types of sp² carbon atoms at $\delta = 135$ and 159 ppm can be distinguished in the ¹³C NMR spectrum, assigned to free sp² carbon and to the sp² carbon bonded to nitrogen, respectively. The same carbon species were found in amorphous carbon nitride films, theoretically calculated for nitrogen doped graphite and recently experimentally verified for carbon-rich SiCN ceramics [32, 33, Mera G, Riedel R, Poli F, Müller K, private communication].

In ¹³C solid state MAS-NMR (Figs. 4b, e) sp²-hybridized species were evident only in high temperature treated materials (MK at 700 °C and Ceraset at 600 °C). From EPR measurements sp²-hybridized carbon radicals were found at lower temperatures. This difference was assigned to the lower sensitivity of MAS-NMR compared to EPR. The experimental NMR and EPR results are in accordance with the optical properties of our samples, where the yellow and brown colors indicated the presence of free sp² carbon in different concentrations.

Conclusions

In conclusion, we demonstrated that heat-treated polysiloxanes and polysilazanes show an appreciable photoluminescence. The maximum visible fluorescence emission intensity is obtained with a heat treatment at 500–600 °C. The fluorescence properties can be correlated to structural changes and to the formation of radicals and carbon sp² associated with the annealing of the polymer materials. Further investigations are currently carried out in order to entirely clarify the fluorescence mechanisms.

The excitation range of the characterized materials meets the excitation range of UV conversion LEDs. The poly(methyl)silsesquioxane reveals white luminescence after annealing at 500 and 600 °C while the poly(urea-ethylvinyl)silazane heat-treated at 500 °C exhibits emission in the blue-green range and is transparent. However, the processing temperature is still too high for direct molding in LEDs. Therefore, our future work is directed to suitable

functionalization of the polymers in order to obtain luminescence emission in the visible range at lower temperatures.

Nevertheless, starting from cheap and non toxic commercial polysiloxanes and polysilazanes is a promising strategy in order to obtain thermally stable and easy-to-process light converting materials for LED applications.

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