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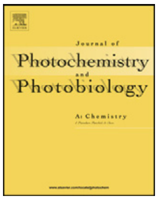

Synthesis, photophysical properties and thermal relaxation processes of carbazolyl-labeled polysiloxanes

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ABSTRACT

The photophysical properties of a fluorescent silicone prepared by a hydrosilylation reaction from poly(dimethylsiloxane-*co*-methylhydrogensiloxane) terminated by dimethylhydrogensilyloxy groups, poly(dimethylsiloxane-*co*-methylvinylsiloxane) terminated by dimethylvinylsilyloxy groups and 9-vinylcarbazole, as the luminescent group, have been studied under steady-state fluorescence and time-resolved conditions. At low temperature both steady-state fluorescence and phosphorescence spectra of isolated species are observed. Phosphorescence is quenched at temperatures higher than 150 K indicating that the environments where the carbazolyl moieties are located are very flexible, as expected for silicones. Fluorescence decays and phosphorescence (at 77 K) showed typical carbazolyl lifetimes and no rise-time was observed, which is consistent with the absence of excimer emission. The temperature dependence of the emission can be used to determine the polymer relaxation processes and transitions ($T_\gamma = 80–100$ K, $T_g = 130–150$ K and $T_m = 220$ K), these last two comparable with those observed by differential scanning calorimetry.

1. Introduction

Silicones or poly(organosiloxane)s (R_2SiO) form a wide class of very flexible, thermally and chemically stable and atoxic polymers that have an enormous variety of applications [1,2]. They can be synthesized with several chain lengths and lateral substituents, with cyclic or linear chains, and as polymeric networks [1,3]. Among their multiple applications, some related with their higher viscosity are becoming important in the microelectronics field [4] as a preformed mask for further deposition processes, a flexible substrate and an active medium, when additional components are dissolved in the silicone before the polymerization reaction. One particular field where electronic applications of polysiloxanes have been developed is related with organic and polymeric light emitting devices and sensors [4]. Poly(organosiloxane)s are well known materials with excellent adhesive properties in several types of substrates [3].

Polyvinyl carbazole is a polymer frequently used in organic electronics since it is a well known material with hole injecting characteristics [5–8]. Although polyvinyl carbazole is an intrinsically electroluminescent material, its efficiency is very low [8]. Because of this poor electroluminescent property, new carbazole-based polymers have been prepared [6], they have been used in blends either with other inert [8–11] or with other more efficient electroluminescent materials [12]. Either in blends or in multiple layer devices, carbazole-based polymers are used as an efficient hole injection layer in the electroluminescent devices [8].

Silicones are generally neither photoluminescent nor electroluminescent materials. However, they can be chemically modified to become luminescent [13] or electroluminescent material [14–16] The photophysical properties of the silicone-based luminescent groups do not follow exactly the same behavior as the carbon-based luminescent polymers because of the larger silicon–carbon or silicon–oxygen distances and angles [17], compared with the carbon–carbon bond distances and angles. In particular, the photophysical properties of carbon-carbazolyl-based polymers are very complex, [18–21] due to the particular ability to form excimers [19–21], which requires a very specific orientation of the two carbazolyl groups and a coplanar arrangement of the rings with an interplanar distance around 3 nm. Because of this specific orientation and interplanar distance, the formation of excimer species can probe both the polymer chain mobility and the interchromophoric distances and orientations [22–24].

Here, we describe the synthesis of a carbazolyl-silicone based polymer as a material which may combine the moldable and elastomeric properties of the silicone and the hole injection property of the carbazolyl groups to be used in flexible electroluminescent devices. This synthesis was carried out by a hydrosilylation reaction catalyzed by platinum complex, from a mixture of

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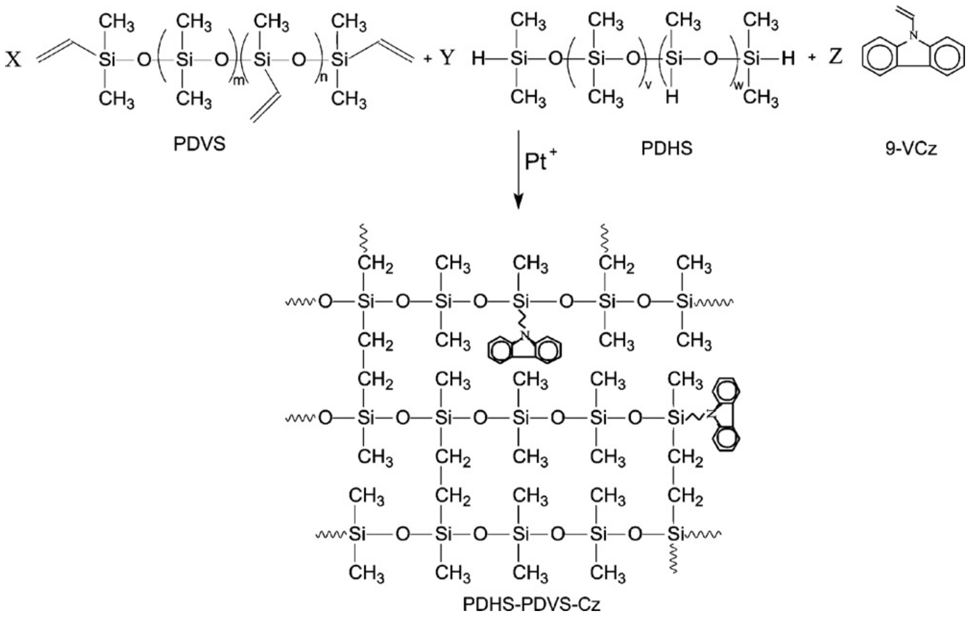

Scheme 1. Scheme for the hydrosilylation reaction of PDHS, PDVS and 9-VCz producing PDHS-PDVS-Cz polymeric network.

poly(dimethylsiloxane-*co*-methylvinylsiloxane) dimethylvinylsilyloxy terminated, poly(dimethylsiloxane-*co*-methylhydrogensiloxane) dimethylhydrogensilyloxy terminated and 9-vinyl carbazole, rendering a silicone network with lateral carbazolyl moieties. The photophysical properties of the silicone-carbazolyl network are presented. For comparison of the physical and photophysical properties, we also prepared a network containing 9H-carbazole-9-ethanol (9-EtCz) as a guest.

2. Experimental

2.1. Materials

Poly(dimethylsiloxane-*co*-methylhydrogensiloxane) dimethylhydrogensilyloxy terminated (PDHS), $HMe_2SiO\text{-}[SiMe_2O]_n[SiMeHO]_m\text{-}SiMe_2H$, with $n \gg m$ and $\overline{M}_n = 2555\,\mathrm{g\,mol^{-1}}$ and poly(dimethylsiloxane-*co*-methylvinylsiloxane) dimethylvinylsilyloxy terminated, $(CH{=}CH_2)Me_2SiO\text{-}[SiMe_2O]_v[SiMeCH{=}CH_2O]_w\text{-}SiMe_2(CH{=}CH_2)$, PDVS, with $v \gg z$ and $\overline{M}_n = 14, 529\,\mathrm{g\,mol^{-1}}$, were supplied by Dow Corning Inc. The structures and reaction are in Scheme 1. The hydrosilylation reaction was catalyzed by a platinum divinyltetramethyldisiloxane complex (platinum catalyst, 3–3.5% platinum concentration in poly(dimethylsiloxane) terminated by dimethylvinylsilyloxy group), purchased from Gelest (Karlsruhe, Germany). The 9-vinylcarbazole (9-VCz, 97%), 9H-carbazole 9-ethanol (9-EtCz, 97%) (as a model for the photoluminescence study) and *n*-hexane (HPLC grade), were purchased from Sigma–Aldrich. All materials were used as received. Two materials were studied: the network with pendant carbazolyl groups (PDHS-PDVS-Cz) and the network with 9-EtCz as a guest (PDHS-PDVS/9-EtCz). The relative molar ratio of the two silicones and the carbazole units were 1:1:10^{-3} PDHS:PDVS:Cz, and the procedure was the same showed in Ref. [13].

It was also produced a luminescent silicone fluid derived from PDHS:Cz (1:2 molar ratio) which was used as a model for NMR studies. Under this condition the NMR signals have enough intensity to identify all of the groups involved with the reaction. 9-VCz was initially dissolved in 10 mL of n-hexane, followed by addition of the platinum catalyst, under stirring. Then, the PDHS was added into the solution. The reaction was performed under argon atmosphere, under stirring for 24 h at 333 K to reach the equilibrium and the solvent was removed by reduced pressure.

2.2. Methods

Infrared spectra (FTIR) of the samples deposited on a NaCl substrate were recorded from 4000 to 600 $\mathrm{cm^{-1}}$ (2 $\mathrm{cm^{-1}}$ of resolution) with a Nicolet model 520 instrument using the attenuated total reflection (ATR) method at an angle of 45°.All NMR spectra were recorded on a Varian INOVA-500 spectrometer.^{29}Si NMR spectra were obtained in $CDCl_3$ at 298 K and TMS as standard solvent at 100 MHz, applying a 45° excitation pulse with a relaxation delay of 5 s. The ^{13}C NMR distortionless enhanced by polarization transfer (DEPT) spectra were recorded at 125 MHz.

Swelling measurements were performed in toluene, following ASTM D47 [25] and as described elsewhere [13].

The thermal transitions of the films were determined by differential scanning calorimetry (DSC), under an argon atmosphere, on a model DSC 2910 from TA Instruments. Initially the sample was cooled from room temperature to 123 K at a rate of 10°/min and heated at the same rate from 123 K to 423 K. A sample of approximately 10 mg was used.

Steady-state photoluminescence spectra at room temperature were recorded using an ISS-PC1, $\lambda_{exc} = 290$ nm emission from 310 to 450 nm. Slits allow the spectral resolution of ±0.5 nm. Samples were sealed in a quartz tube under argon. Spectra were recorded in a back-face orientation.

Steady-state emission spectra from 20 to 410 K at 10 K intervals were recorded with the film sample in a APD Cryogenics cryostat with a lab-made spectrum acquisition system, described elsewhere [26]. Samples inside the cold finger of the cryostat were held between two quartz windows and maintained under a dynamic vacuum of 10^{-4} torr. This spectral set up operates with a Spex 0.5 m monochromator with slits adjusted micrometrically to allow a resolution of 0.2 nm.

Fluorescence decays of the same samples were obtained in a time-resolved FL-900 spectrofluorimeter (Edinburgh Analytical Instruments, Edinburgh), using the time correlated single photon counting (TCSPC) method. λ_{exc} was 290 nm and the emission was collected at 350 nm. Samples were sealed in a quartz tube under nitrogen. The observed fluorescence decay, $R(t)$, is given by the convolution of the hydrogen lamp pulse and the sample signals and the lifetimes were analyzed by the exponential series method with software supplied by Edinburg [27,28]. Ludox® was used as scatterer.

Phosphorescence spectra and decays were recorded for solution and films saturated with N_2 in sealed quartz vessels with a F-4500 Hitachi Spectrometer working with a 300 W pulsed xenon lamp. Measurements were performed at room temperature and at 77 K.

3. Results and discussion

3.1. Material characterization

The synthesis of the PDHS-PDVS-Cz silicone network with pendant carbazolyl groups (Scheme 1) is based on the hydrosilylation reaction of the Si–H group from PDHS with both the vinyl groups from PVDS and 9-VCz. Since the PDHS has terminal and lateral Si–H groups and PDVS has terminal and lateral vinyl groups, a polymeric network was produced. The crosslinking degree is controlled by the relative amount of the reactive groups. In addition, in the PDHS-PDVS-Cz silicone network the carbazolyl groups can be attached as a terminal or a lateral group and the Cz amount is controlled by the initial molar ratio. In the present case, the initial molar ratio of the reactants was PDHS:PDVS:Cz = 1:1:10^{-3}.

Since the relative amount of fluorescent groups in the silicone network is small, the incorporation of the carbazoloy moieties cannot be detected by FTIR. However, the synthesis of the silicone network (PDHS-PDVS-Cz) (Scheme 1) could be followed by the disappearance of the Si–H absorption (2127 cm^{-1}) from PDHS (Supporting information, Fig. S1). The reaction progressed until the complete disappearance of this band.

Evidences of the chemical reaction were also demonstrated by the absence of the peak at −9.34 ppm in the ^{29}Si NMR spectra. This peak was assigned to the $-OSi(CH_3)_2H$ end-groups resulted from the consumption of the Si–H by the hydrosilylation reaction with 9-VCz (Supporting information, Figs. 2 and 3). We also observe the appearance of the peaks at: 7.0 ppm, associated with type M = $CH_2CH_2Si(CH_3)_2O-$ segments [1], and peaks at −21.4 ppm and −22.3 ppm, associated with type D = $(CH_3)_2Si(O-)_2$ segments. In the ^{13}C NMR DEPT-135 the CH_2 group from $CH_2{=}CH-$ shifts from 100–110 to 15–40 ppm in the 9-VCz, due to the addition of Si–H group (Supporting information, Figs. 4 and 5).

The average molar mass between crosslinking points ($\bar{M}_C$) and crosslinking density of the silicone networks (n_{FR}) show no differences for both PDHS-PDVS-Cz and PDHS-PDVS/9-EtCz materials (Table 1), due to the low amount of Cz introduced in the polymeric network. Thus, they are independent of the attachment of the Cz luminescent groups.

Comparison between the thermal transitions by DSC of both PDHS-PDVS/9-EtCz and PDHS-PDVS-Cz samples showed a small change of the baseline at around 153 K, which was attributed to the glass transitions of these materials, T_g; an exothermic peak at 192 K assigned to the crystallization of the linear silicone segments of the network, and an endothermic peak at 237 K corresponding to the melting of these crystalline domains (Fig. 1, Table 1). No differences in these temperatures were noted for the two samples, indicating that the photoluminescent groups are not disturbing the thermal properties of these materials. Similar transitions are observed in other silicone polymers [1,3,13].

Table 1
Equilibrium swelling ratio, $S_{R(eq)}$, crosslinking density, n_{FR} and, average molecular weight, $\overline{M}_c$, Between crosslinking points for polysiloxanes. Swelling agent: toluene.

Samples	$S_{R(eq)}$	n^{RF} (10^{-4} mol cm^{-3})	$\overline{M}_c$ (g mol^{-1})
PDHS-PDVS-Cz	3.72 ± 0.02	3.3	2947
PDHS-PDVS/9-EtCz	3.17 ± 0.04	3.2	3040

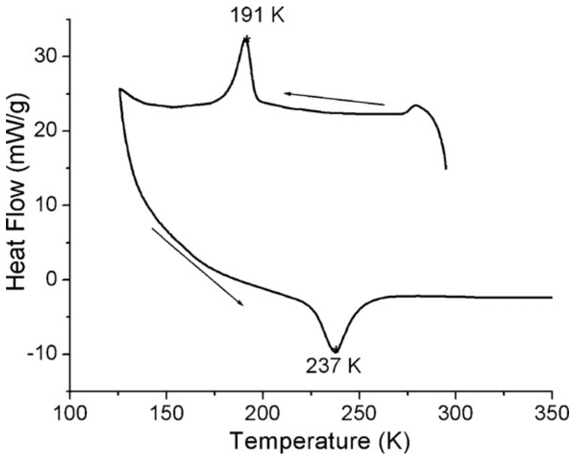

Fig. 1. DSC curve for PDHS-PDVS/9-EtCz. Heating scan 10 °/min; cooling scan 10 °/min.

3.2. Photophysical characterization

Initially, the luminescence spectra of the 9-VCz solution (1×10^{-5} mol L^{-1}) were studied in *n*-hexane and in PDHS (Fig. 2a).

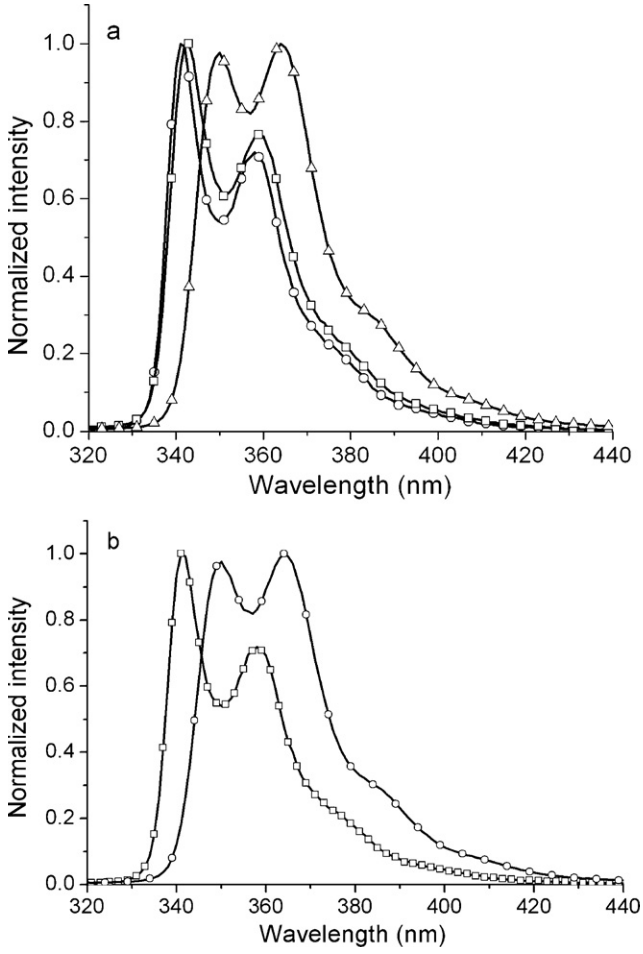

Fig. 2. Normalized fluorescence emission of: (a) 9-VCz in (○) in hexane and (□) in PDHS and of (△) 9-EtCz in PDHS solutions. Concentration of 9-VCz and 9-EtCz = 1×10^{-5} mol L^{-1}; (b) (□) 9-VCz in PDHS solutions (1×10^{-5} mol L^{-1}) and (○) PDHS-PDVS-Cz. λ_{exc} = 290 nm. Spectra taken at room temperature.

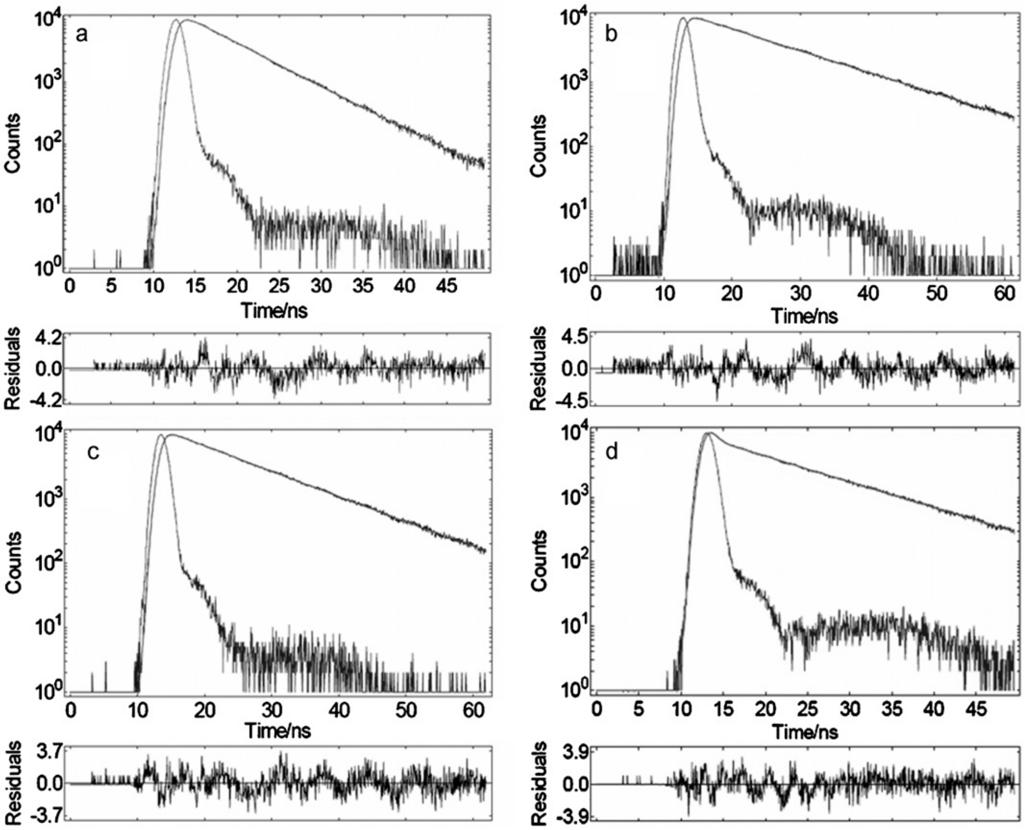

Fig. 3. Fluorescence decays for: (a) 9-VCz in PDHS solution (1×10^{-5} mol L^{-1}); (b) PDHS-Cz; (c) PDHS-PDVS-Cz; (d) PDHS-PDVS/9-EtCz. λ_{exc} = 290 nm; λ_{em} = 350 nm. Measurements at room temperature.

The emission is composed of a vibronic progression with the 0–0 band located around λ_{em} = 341 nm. There is a small red-shift of the fluorescence spectrum of 9-VCz in PDHS (λ_{em} = 343 nm) when compared to *n*-hexane (λ_{em} = 341 nm), which can be explained by the higher polarity of PDHS. As we can see, under the experimental conditions no excimer emission is observed and the emission with a well resolved vibronic structure, characteristic of the carbazolyl groups, is present [18–23]. For comparison, we also recorded the fluorescence spectrum of 9-EtCz dissolved in PDHS (1×10^{-5} mol L^{-1}) (Fig. 2a) which shows a well structured red-shifted band characteristic of carbazolyl groups, with the 0–0 band at λ_{em} = 350 nm. Therefore, when changing from a vinyl to an alkyl substituent, the fluorescence emission of carbazolyl is red-shifted.

Steady-state fluorescence spectroscopy at room temperature of the PDHS-PDVS-Cz network showed an emission with two well resolved vibronic peaks at λ_{em} = 350 nm and λ_{em} = 364 nm (Fig. 2b), similar to the emission of the 9-EtCz in PDHS solution (1×10^{-5} mol L^{-1}), where two well resolved vibronic bands were observed at λ_{em} = 350 nm and λ_{em} = 363 nm. As we also can see, both are red-shifted compared to the spectrum of 9-VCz in PDHS, indicating that the hydrosilylation reaction occurred effectively. Therefore, fluorescence spectroscopy gave additional evidence that the carbazolyl groups are incorporated in the polymer chain due to the remarkable change of the emission after the reaction. In addition, a broader spectrum for the luminescent group attached to the polymer chains was observed, which can be explained by the conformational disorder of the silicone network [13,19].

Initially, the fluorescence lifetime at room temperature was determined for 9-VCz in PDHS solution (1×10^{-5} mol L^{-1}) (Fig. 3a). The curve profile was well represented by a mono-exponential function when carbazol molecules are dissolved in PDHS with an emission decay of τ_F = 6.15 ± 0.01 ns (Table 2). When the carbazolyl groups are attached to the polymeric chain forming the PDHS-Cz, the decay becomes bi-exponential with a longer component with τ_{F1} = 12.98±0.06 ns (~95.7%) and a faster component, with τ_{F2} = 5.21 ± 0.50 ns (~4.30%) (Fig. 3b, Table 2). Because of the distribution of the SiH groups preferentially as terminal groups in the PDHS chains, the PDHS-Cz chain is practically linear forming a viscous fluid at room temperature (glass transition temperature is 153 K). Carbazolyl moieties are predominantly located as terminal groups. In this viscous fluid, the macromolecule undergoes a coil conformation and in this conformation some carbazolyl groups may be oriented within the helix becoming more protected to the environment, some others may be oriented more externally being lesser protected. In other words, there is a non-uniform distribution of the environments around the lumophores, which is very usual in polymer systems with pendant lumophores [29]. Since no excimer emission was observed, we do not expect a higher local concentration of the lumophores, which do not exclude the possibility of quenching either by close proximity of some carbazolyl moieties in non-excimeric orientation or by residual oxygen in N_2 saturated atmosphere. Since these are fluid systems, quenching by dynamic processes are one of the possibilities at room temperature, since ground state aggregates are not observed.

Table 2
Fluorescence lifetimes for: 9-VCz in PDHS solution (1×10^{-5} mol L^{-1}) (PDHS/9-VCz), PDHS-Cz, PDHS-PDVS-Cz and PDHS-PDVS/9-EtCz. λ_{exc} = 290 nm, λ_{em} = 350 nm.

Samples	τ_{FL1} (ns)	B_1 (%)	τ_{FL2} (ns)	B_2 (%)	χ^2
PDHS/9-VCz	6.15 ± 0.0	100	–	–	1.226
PDHS-Cz	12.98 ± 0.06	95.7	5.21 ± 0.50	4.30	1.515
PDHS-PDVS-Cz	11.21 ± 0.19	93.6	7.16 ± 1.78	6.4	1.246
PDHS-PDVS/9-EtCz	10.60 ± 0.01	90.5	0.31 ± 0.01	9.5	1.146

Therefore, we assign the longer component value coincident with those that contain carbazol units as an isolated lumophore, while the shorter component probably results of some type of quenching of carbazol units [15–24,27]. The fit of this decay curve by an exponential function is very poor, which indicates that the system undergoes very complex dynamical photophysical processes after excitation.

For the polymeric network (PDHS-PDVS-Cz), the emission can be reasonably fitted by a biexponential function with a longer component $\tau_{F1} = 11.21 \pm 0.19$ ns (~93.6%) and a faster component of $\tau_{F2} = 7.16 \pm 1.78$ ns (~6.40%). We also measured the decay curve for the 9-EtCz as guest in the PDHS-PDVS/9-EtCz network (Fig. 3d). Again the decay can be fitted by a bi-exponential function with one longer $\tau_{F1} = 10.60 \pm 0.01$ ns (~90.5%) and one faster $\tau_{F2} = 0.31 \pm 0.01$ ns (~9.5%) component. Guest decays are faster than carbazolyl attached to chain, indication that they are more susceptible to quenching processes. PDHS-PDVS-Cz is a crosslinked network, where the PDHS is the component involved with the crosslinking and the Cz can be located either in the terminal positions of the network or within the cage of the crosslinked matrix. Therefore, the distribution of the Cz components is again non-uniform, some are more susceptible to quenching, some are more protected. Although the mobility in crosslinked network is more hindered, some local mobility is still operating since the polymer is above the glass transition temperature.

For comparison, when carbazolyl groups are attached to poly(methyl methacrylate), a bi-exponential decay with a slower ($\tau_{F1} = 12.21$ ns) and a faster ($\tau_{F2} = 3.53$ ns) components is also observed with a small contribution of a faster component [19]. We suspect that there are at least two reasons for the presence of the faster decays in polysiloxanes: (i) since they are polymers with high chain mobility at room temperature ($T_g \sim 150$ K), compared with the polyacrylates ($T_g \sim 380$ K) [19], the possibility of quenching is greater; (ii) due to the synthetic process used here, there is a possibility of having some terminal carbazolyl groups (more susceptive to quenching) and groups located in inner cavities of the network between crosslinking points (less susceptive to quenching). Thus, a bi-exponential decay function is required to represent the emission decay.

In addition to the fluorescence emission, we also recorded the phosphorescence spectra at 77 K of the PDHS-PDVS-Cz and the PDHS-PDVS/9-EtCz samples (Fig. 4, Table 2). At room temperature, only fluorescence emission was observed. Nevertheless, the luminescence at 77 K gave a fluorescence emission in the range between $\lambda_{em(FL)} = 330$ and $\lambda_{em(FL)} = 400$ nm and a phosphorescence emission at lower energy, with vibronic structure in the range of $\lambda_{em(Ph)} = 400–550$. The phosphorescence decays followed mono-exponential behavior (Fig. 5) with a lifetime about $\tau_{Ph} = 3.15$ s, in agreement with several other reports for carbazol compounds [19,30,31]. We do not observe differences for this decay when carbazol is attached or is a guest in these silicone networks. It is worth noting that the relative intensity of the phosphorescence emission measured using the millisecond time-resolved spectroscopy of carbazolyl groups is poly(methyl methacrylate) is greater than in the silicones present here although the lifetime is a little faster ($\tau_{Ph} = 1.2$ s) [19].

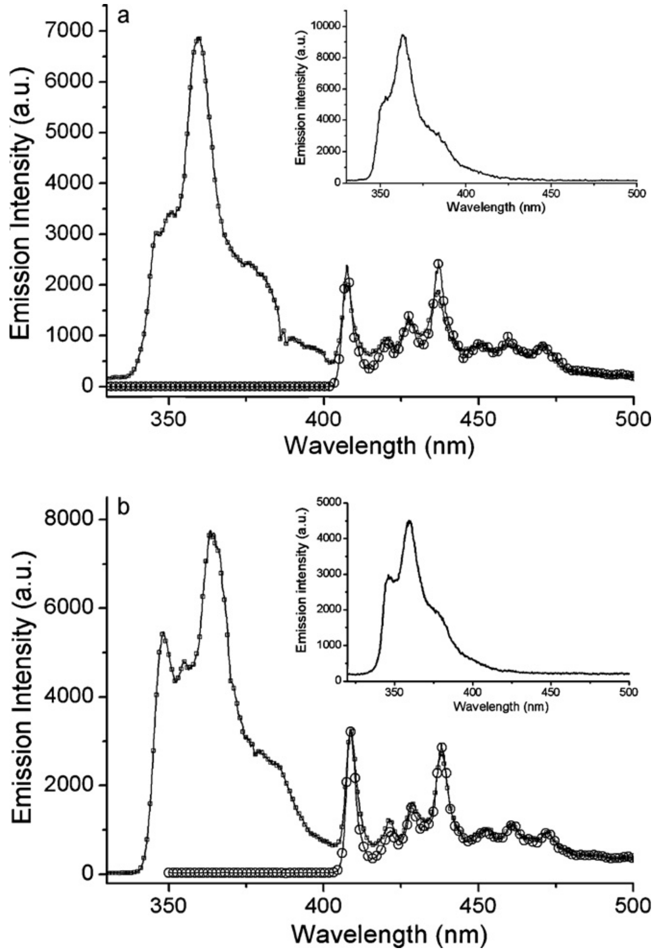

Fig. 4. Steady-state (-□-) and millisecond time-resolved phosphorescence (-○-) of: (a) PDHS-PDVS/9-EtCz as a guest (0.01% w/w) and (b) PDHS-PDVS-Cz, at 77 K and at room temperature (inset) ($\lambda_{exc} = 295$ nm).

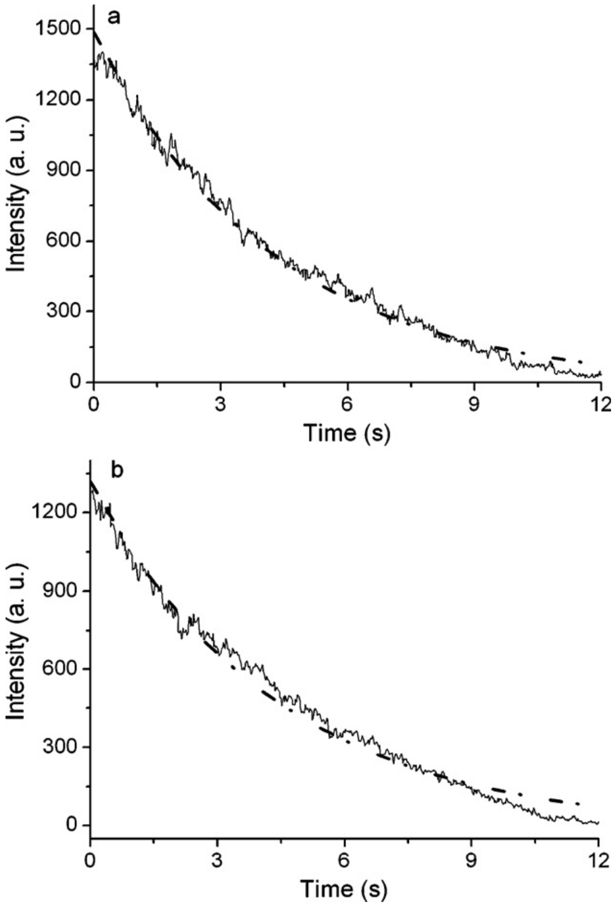

Fig. 5. Phosphorescence decays at 77 K of: (a) PDHS-PDVS/9-EtCz (0.01% w/w) and (b) PDHS-PDVS-Cz. $\lambda_{exc} = 290$ nm; $\lambda_{em} = 440$ nm.

As we can see in Fig. 4, no excimer emission was observed either at 300 K or at 77 K for either materials containing guest and attached carbazol. One possible reason for the absence of excimers is that the relative amount of the carbazolyl units is small. The other is that the distance or relative orientation of the lumophores is not suitable for the excimer formation. In order to get some insight into at this result, we simulated the geometry of a silicone chain with two carbazolyl groups attached at the end of a siloxane chain containing 17 $Si(CH_3)_2O$ mers, using HyperChem v6.3 software (Fig. 6) [32]. This is a very simple quantum mechanical semi-empirical calculation providing only qualitative visualization of the electronic ground state geometry. For the proposed structure we do not obtained any geometrical possibility of interaction between two carbazolyl moieties. Although very suggestive, more precise theoretical methodologies are required to prove a good description of the geometrical orientation and relative distances for carbazole-based silicones.

3.3. Temperature effects on the steady-state luminescence

The evolution of the emission intensity as a function of the temperature was measured in the range from 20 to 400 K for both samples, PDHS-PDVS/9-EtCz and PDHS-PDVS-Cz (Fig. 7). The emission spectra at lower temperatures for these samples are composed by two bands, one at higher energy attributed to fluorescence and other at lower energy attributed to phosphorescence. The spectral profile is very similar for both samples indicating that guest and attached carbazolyl groups are distributed in the silicone network without aggregation. Apparently, no excimer emission was observed. The intensity of these spectra decreases with the increase of the temperature. This decrease as a function of the temperature was analyzed using three sets of data: (i) the entire emission taken the integral over the entire spectral range (area under the

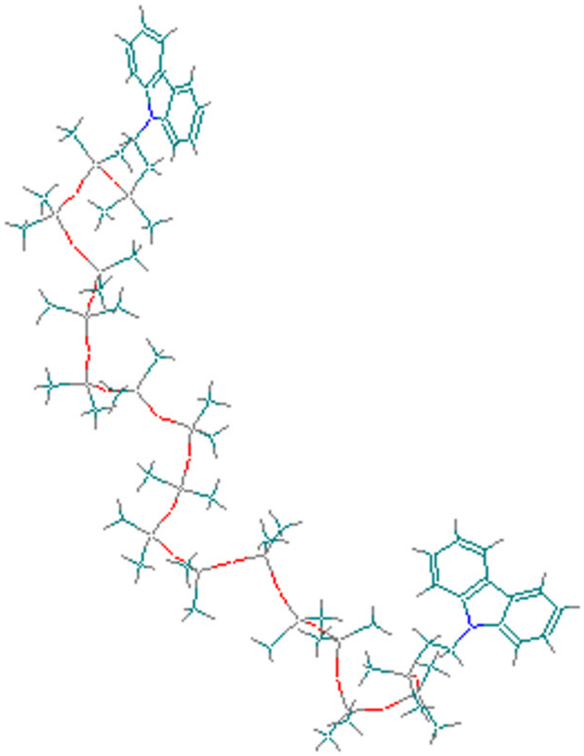

Fig. 6. Simulated molecular structure of the PDHS-Cz using 17 mers of $Si(CH_3)_2O$.

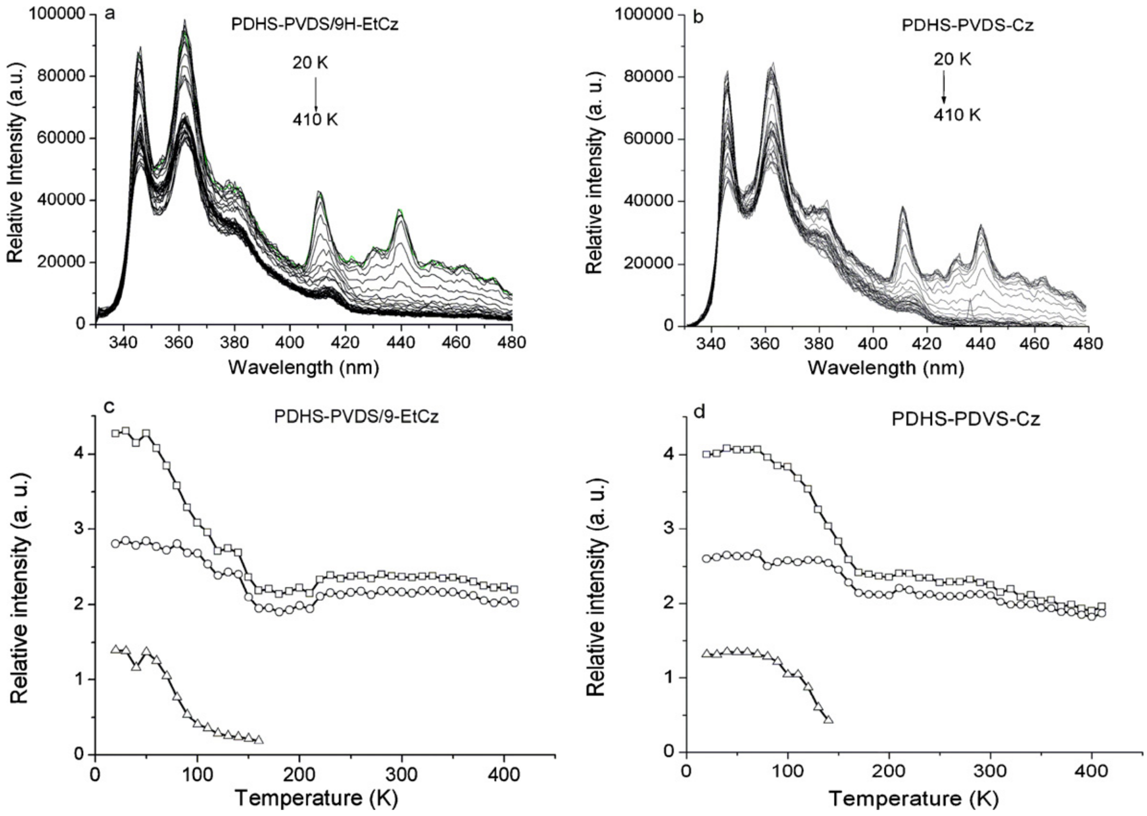

Fig. 7. Steady-state emission spectra at several temperatures from 20 to 410 K and integrated intensity of the total emission band (□), fluorescence band ($\lambda_{em(FL)} = 330–400$ nm) (○) and phosphorescence band ($\lambda_{em(Ph)} = 405–500$ nm) (△) for PDHS-PVDS/9-EtCz (a and c) and PDHS-PDVS-Cz (b and d). Measurements in the interval of 10 K. $\lambda_{exc} = 290$ nm.

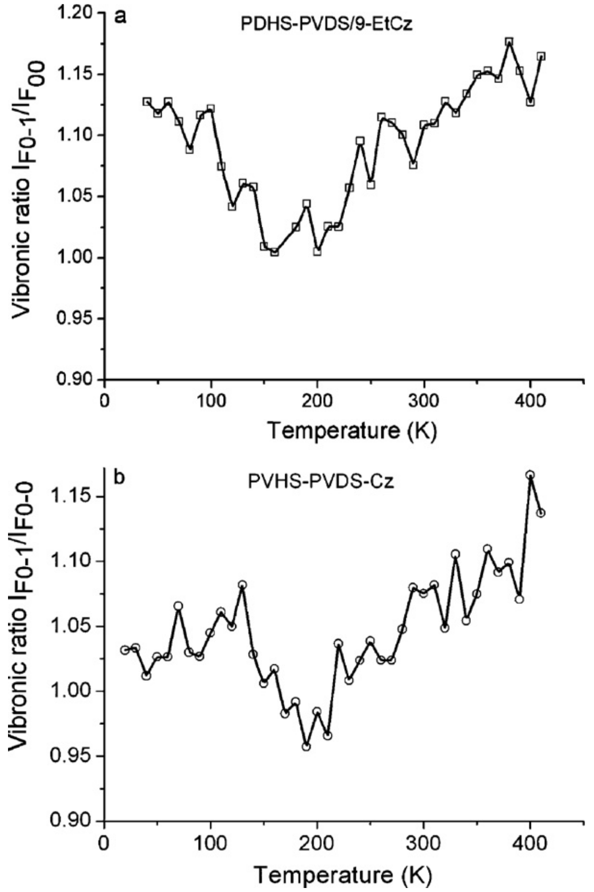

Fig. 8. Vibronic intensity ratio $I_{F0\text{-}1}/I_{F0\text{-}0}$ of the fluorescence band as a function of the temperature.

curve from λ_{em} = 330 nm to 500 nm) (Fig. 7). (ii) The total intensity of the fluorescence emission taking as the integral over the region from $\lambda_{em(FL)}$ = 330 nm to 400 nm and the total intensity of the phosphorescence (from $\lambda_{em(Ph)}$ = 405 to 500 nm); (iii) using the vibronic intensity ratio between the 0–0 and the 0–1 bands of the fluorescence emission (Fig. 8).

Taking into account the profile of the curves of the intensity versus temperature, there are specific temperature values where slope changes are observed. These temperatures can be associated to the polymeric relaxation processes that are inducing additional non-radiative pathways for emission deactivation [13,17,19,33,34]. Examining the curve profiles for the two samples, we can see that there are some slope changes which are not exactly at the same temperatures. In general, for the carbazolyl guest (Fig. 7c) the temperatures are lower than for the carbazolyl pendant groups (Fig. 7d). For example, when the total integrated intensity is considered, the curve for the guest undergoes the first slope change at 50 K and the pendant group at 80 K. In addition, at this temperature range, the behavior of the integrated intensity is strongly influenced by the phosphorescence intensity which is completely suppressed at above 150 K, for both samples. Polymeric relaxation processes in the lower temperatures can be assigned to rotational motion of small segments of the polymeric chain, usually associated with terminal groups. We will call here as T_γ.

Around 130 K there is an additional slope change and then, from 150 to 220 K, the emission intensity remains practically constant for the sample containing the guest 9-EtCz and from 150 to 280 K, for the sample with pendant carbazolyl. Looking at the DSC data, the glass transition and the melting point (T_g = 153 K, T_m = 237 K) occur in this temperature range. Values of glass transition temperature for silicones were observed around 145 K [1,3,13]. It is also important keep in mind that for silicones the heat flow in the glass transition is very weak and the visualization of the glass transition by conventional thermal methods is usually very difficult. Finally, we observe another change of the fluorescence intensity around 220 K attributed to the melting process. As we can also see, the melting temperature is more clearly observed for the guest than for the pendant groups. The total amount of the carbazolyl moieties is constant and certainly independent of the temperature. It does not mean that the distribution is uniform along the polymer matrix when the silicone is frozen because it becomes partially crystallized. Since the pendant groups or the carbazolyl guests cannot be located in the interior of the crystalline phase, there is a non-uniform concentration of the lumophore along the entire frozen matrix. This creates a higher relative concentration in the amorphous phase, some concentration in the interface between the crystalline and amorphous phases and a completely absence of lumophores within the crystals. Both lateral groups or guests in semicrystalline polymers are always excluded from the interior of the crystalline phase [35–37]. Therefore when the crystalline part of the material melts, there is a dilution of the lumophores over the entire matrix, although the total amount is constant. It is noteworthy that after the melting point, there is a small increase of the emission intensity, which can be explained by a dilution effect of the luminescent groups by the entire mass of the polymeric network. This dilution decreases the possibility of the static and dynamical quenching of the excited state groups. The reason for the different sensitivity to the melting when we use lateral or guest lumophores is still quite speculative, but we may consider that their distribution in the matrix is different: guests may be better distributed in the amorphous and in the interfaces crystalline-amorphous while pendant are occupying the amorphous phase. Movements of the chains during the melting strongly interfere with the interface where some guests are probably located.

The temperature dependence of the fluorescence emission can also be analyzed in terms of the relaxation processes of the Franck–Condon (FC) excited state. We can assume that the emission is originated from non-relaxed FC states only when the material is completely frozen [38]. Under this condition, the emission efficiency is only controlled by intrinsic non-radiative processes, such as internal conversion and intersystem crossing in diluted systems in the absence of other bimolecular processes [39]. In a frozen system, the molecular geometry in both the electronic ground state and the electronic excited state is the same, and thus the vibronic progression of the emission and of the absorption bands will not be modified. One type of parameter that describes this behavior is the Huang–Rhys factor S, which constitutes a measurement of the changes of the coordinates of the equilibrium geometry in both states involved in the electronic transition [40]. Under the distorted harmonic potential approximation the Huang–Rhys parameter is given by the equation:

$$S = \frac{I_{0,1}}{I_{0,0}}$$

where $I_{0,1}$ and $I_{0,0}$ are the vibronic intensities of the 0–1 and 0–0 bands, respectively, at $\lambda_{em(0-1)}$ = 362 nm and $\lambda_{em(0,0)}$ = 346 nm for both samples. Thus, taking the vibronic intensities of the 0–0 and 0–1 bands from Fig. 7a and b, we can estimate the S parameter for every temperature. As we can see the dependence of the S-factor with the temperature (Fig. 8) is relatively small when compared with more flexible materials such as conjugated polymers [41]. Although small, we observe some slope changes of the curve profile at the temperatures which were associated to the polymer relaxation processes: T_γ = 100 K; T_g = 160 K and T_m = 220 K. The increase of the S-factor at temperatures above melting is associated to the gain of polymeric chain mobility, inducing relaxation processes of the FC states of carbazolyl excited state. In other words, the gain of polymeric matrix mobility creates a new channel for the relaxation of the FC excited states and the luminescent groups will emit from them. Consequently, there is a relative intensification of the 0–1 vibronic component compared with the 0–0 band. We can also see from Fig. 8 that the changes produced in the guest represented by the slope changes are more pronounced and occur at lower temperatures than for pendant groups, indicating that they are located in more flexible environments.

Thus, combining all the spectroscopic information, we conclude that the carbazolyl groups are sensitive to the environment and guest or pendant groups are not located or sensing exactly the same processes at the same temperatures, but both can identify polymeric relaxation processes in temperatures near (not equal) to those processes identified by other methods.

4. Conclusions

A luminescent carbazolyl-silicone network was synthesized by a hydrosilylation reaction. This material emits fluorescence and at lower temperatures also phosphorescence, but no excimer emission. These groups can be used to probe for polymeric chain relaxation processes whose temperatures were similar to those determined by other methodologies. Phosphorescence emission was able to detect a very low relaxation process below the glass transition and becomes completely quenched above T_g. On the other hand, the fluorescence signals can detect all polymeric relaxation processes including the glass transition and the melting processes. Guest molecules are more sensitive to the relaxation processes at lower temperature and to the melting point, indicating that the distribution of the disperse molecules is not the same as the distribution of the pendant groups. The gain of mobility of the luminescent molecules induced by the polymeric matrix relaxation can be discussed by using the Huang–Rhys factor that is related to the generation of emission from the relaxed Franck–Condon state.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.11.003.

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