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In situ synthesis of photoluminescent films of PVC, doped with Ce^{3+} ion

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Abstract

In this paper we report on the *in situ* synthesis of photo luminescent and patterned polyvinyl chloride (PVC) films, doped with cerium chloride. The precursor of the doping agent is the Tris(2-4 pentanedionate)cerium(III)•$3H_2O$, $Ce(acac)_3$, which absorbs UV and visible light. The PVC is both the photochemical source of chloride ion and the rigid matrix where the $CeCl_3$ luminescent particles are dispersed. The PVC films containing cerium complex in the concentration range 0–3% w/w did not exhibit luminescence over 320 nm. After irradiation at 254 nm, the films of pure PVC exhibited luminescence emission with a maximum at about 420 nm, by excitation at 300 nm, due to the presence of polyenes, likely formed by PVC photodehydrochlorination. In PVC films, containing cerium complex, the HCl photoproduct underwent substitution of $acac^-$, with the formation of $CeCl_3$ and Hacac, detected by XPS and FTIR, respectively. Thus, these films exhibited the luminescence emissions of the cerium chloride at about 360 nm and that of the polyenes at 420 nm, that was evidenced well by excitation at 260 and 300 nm, respectively. The film luminescence appeared after an induction period which was a function of the $Ce(acac)_3$ percentage and which was different for the two emitting species, as resulted by deconvolution of the luminescence band. The film irradiation by using a mask resulted in direct photopatterning. The luminescence emission occurred exclusively from directly irradiated zones. Thus no reaction occurred for the migration of reactive species.

The FTIR analysis of the films, before and after sufficient irradiation to obtain luminescence, did not evidence significant changes in the chemical structure of the polymer and in the surface properties. Thus, this method can be used to provide PVC with luminescence without damaging side effect.

Keywords: Photoluminescence; PVC; Cerium chloride; Film; Photopatterning

1. Introduction

The poly(vinyl chloride) (PVC) is one of the most popular polymers used in the production of household goods, in medical and packaging applications, in the food industry, in the manufacture of protection agents as well as in many industrial branches [1–3], due to its property of easy modification and low production costs. Even if several studies have evidenced that the UV irradiation causes changes in the chemical structure of the polymer [4–6], its photodegradation is not fast enough to classify this polymer as degradable. The main processes include dehydrochlorination with polyene formation, chain scission, crosslinking, oxidation, cyclization and isomerization. Besides this, the UV irradiation can be used to obtain material with specific properties, which can find applications in different fields. For example, the irradiation was used to provide films containing suitable additives [7] with electrical or optical properties.

The present paper reports on the use of a suitable dose of UV light to prepare *in situ* photoluminescent and patterned PVC films, doped with cerium chloride, which are expected to find a potential application as new optical materials [8]. The PVC is the photochemical source of chloride ion and forms the rigid matrix where the $CeCl_3$ luminescent particles are dispersed. The precursor of the doping agent is the Tris(2-4 pentanedionate)cerium(III)•$3H_2O$, $Ce(acac)_3$, which belongs to the class of β-diketonates, compounds important for photochemical investigation because they absorb UV and visible light [9]. Previously, in the context of our work on the use of light as an alternative route to synthesize materials with promising practical application [10–13], we prepared and characterized luminescent

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colloidal particles and nanostructured films of $CeCl_3$ by irradiating the Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)cerium diglyme complex in chlorinated solvents [14].

2. Experimental

PVC (Sigma–Aldrich, FW 48,000) was supplied by Fluka and purified by washing first in hot distilled water and then methanol. tetrahydrofuran (THF) (Sigma–Aldrich) was analytical grade.

Tris(2-4-pentanedionato)cerium(III)$^\bullet$$3H_2O$, $Ce(acac)_3$, was reagent grade and used without further purification. The effective number of H_2O molecules was determined through thermogravimetric analysis. For film preparation, PVC powder (0.4 g) was dissolved in THF (20 mL) and a variable volume of $Ce(acac)_3$ solution in THF, containing complex in the range 0.4–12 mg, was added. The films were obtained by casting the solution onto a Petri dish of area 41 cm^2 where a quartz plate (1.2 cm × 4.5 cm) was placed inside. After slow evaporation of the solvent at room temperature, the sample on the plate was put into a dryer for 48 h.

The films of pure (no doped) PVC and all the films containing cerium complex up to three in weight percentage (0–0.85% in cerium), exhibited transmittance over 98% at 254 nm. The interference fringes were used to calculate the film thickness by the equation [15]:

$$d(\text{thickness}) = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_{D2} - \lambda_2 n_{D1})}$$

where λ_1 and λ_2 are the wavelengths correspondent at two consecutive interference fringes, and n_{D1} and n_{D2} are the refractive indexes for bi-refringent material at 22 °C [16]. In our case, $n_{D1} = n_{D2} = 1.55$. We used films that were about 0.03 mm thickness.

The irradiation was performed using a variable number of low pressure mercury vapour lamps (8 W, Italquartz), with an emission maximum at 254 nm. The films and solutions were irradiated with an intensity light of 3.8 and 11 mW cm^{-2}, respectively. The details of the irradiation equipment have been reported in our previous papers [10–14].

The course of the photochemical changes was monitored by UV-visible, luminescence and FTIR spectroscopy. The photocrosslinking was evaluated by the percentage of insoluble gel obtained by solving the irradiated film in THF and drying residue until a constant weight was obtained.

Ultraviolet-visible absorption spectra were monitored using a double beam Jasco-V560 spectrophotometer.

For the luminescence spectra, a SPEX Fluorolog 111 instrument, equipped with a solid plate sample holder, was used. The spectra were recorded within the linear range of the photo multiplier response. The acquisition mode used was signal/reference (S/R) for the excitation spectra. The integration time and slit width were 0.2 s and 5–5 nm, respectively. In most cases, to compare the luminescence of the samples, the signal of the instrument was reported in the default units (cps) without normalization. The photoluminescence quantum yield of the $CeCl_3$ in PVC matrix were calculated respect to a PVC film containing 0.12% of anthracene as standard, using the relation:

$$\Phi_{sa} = \frac{\text{Area(sa)}}{\text{Area(st)}} \frac{\Phi(\text{st}) A_{\lambda\text{exc}}(\text{st})}{A_{\lambda\text{exc}}(\text{sa})}$$

where sa, sample; st, standard and A, absorbance.

An ultraviolet transilluminator UVTEC was used to evidence the patterned film.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5600 multitechnique system equipped with Al and Mg standard X-ray sources operating at 14 kV and a hemispherical analyser. The electron take-off (θ) was 45° with an acceptance angle of ±7°. XPS binding energy (BE) scale was calibrated by centering the C 1s peak of the “adventitious” carbon at 285.0 eV [17,18].

FT-Infrared spectra (between 400 and 4000 cm^{-1}) were measured using a Fourier transform infrared spectrometer FT-IR 430 JASCO. The spectra resolution was of 4 cm^{-1}.

3. Results and discussion

3.1. Photo reactivity of Ce(acac)$_3$ in solution

The photo reactivity of $Ce(acac)_3$ was tested in protic (CH_3OH), aprotic (CH_3CN, THF) and chlorinated solvents ($CHCl_3$). As expected for β-diketonate of rare earth ions having f–d transitions [19], the complex did not show any fluorescence. As previously found by other authors [20], in CH_3OH, complex solutions of concentration $<10^{-4}$ M exhibited only the characteristic band at about 295 nm, attributable to transition π–π^* in the bidentate (O,O) 2,4 pentanedionate [21]. In CH_3CN, THF and $CHCl_3$, a band with a maximum at 275 nm is present. This band coincides with that of the acetylacetone (Hacac), attributable to intraligand transition of the enolic form of free ligand [22] and could be expected in complexes with monodentate(O-) 2-4 pentanedionate. These findings point to a different rearrangement of the coordination sphere of the complex in aprotic solvents, in accordance with the observed photochemical behaviour. In fact we found that, in CH_3CN and THF the complex exhibited a photochemical reactivity similar to that shown by free Hacac [23]. For UV irradiation, both complex and Hacac spectra decreased without any maximum shift, suggesting a ligand degradation to molecules which absorb below 240 nm. In $CHCl_3$, the absorbance decreased, but the maximum shifted towards 295 nm with the irradiation time. On the basis of the previous investigation regarding the behaviour of the diketonates in chlorinated solvents [12,14,24], it is possible that in the $CHCl_3$ the ligand underwent both degradation and gradual substitution, i.e. $acac^-$–Cl^-, by the HCl, photochemically formed from $CHCl_3$. The attack of the chloride ion alters the electronic properties of the central atom and the stereochemical arrangement of the complex, making possible the attack by the bidentate residual $acac^-$. The spectral variations evidenced these two processes occurring at the same time: the ligand degradation, responsible for the absorbance decrease, and the formation of the intermediate mixed ligand complex, $Ce(Cl)_x(acac)_y$, containing bidentate 2-4 pentanedionate(O,O), consistent with the maximum shifting towards 295 nm. The cerium chlorocomplexes

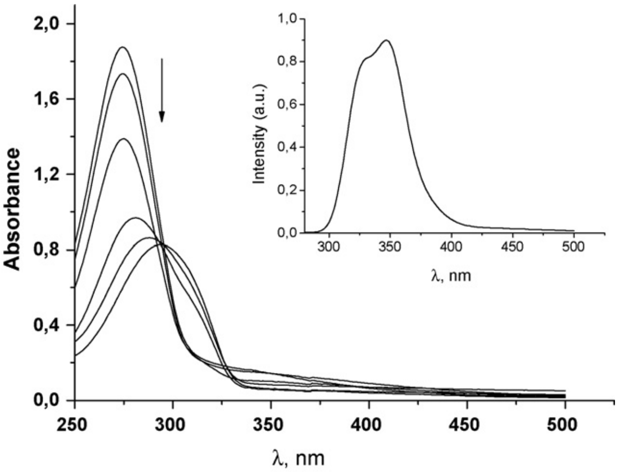

Fig. 1. Spectral changes of $CHCl_3$ solution containing $Ce(acac)_3{\bullet}3H_2O$ irradiated at 254 nm; irradiation times: 0–50 min. Inset: fluorescence spectrum of the above solution irradiated for 50 min.

formation was confirmed by the appearance of the typical fluorescence of the Ce^{3+} ion [25], increasing with irradiation time (Fig. 1).

3.2. PVC films, doped with Ce^{3+} ion.

With the aim of utilizing the PVC both as a rigid matrix and as the source of HCl, initially we tested this latter possibility by carrying out experiments on the photochemical behaviour of PVC solutions (0.2 M of monomeric units) in THF, irradiated at 254 nm. It was found that after 3 h of irradiation, the solution was clear and did not exhibit any luminescence. By interrupting the irradiation and adding some $Ce(acac)_3$, the typical fluorescence of the Ce^{3+} ion appeared and increased slowly until it reached a constant value. This experiment confirms that PVC is a photochemical source of HCl and that the substitution $acac^-$–Cl^- occurs thermally.

By irradiating THF solutions containing both PVC (0.2 M) and $Ce(acac)_3$ (10^{-4} M), corresponding to 0.4 cerium complex weight percentage, from the beginning of irradiation, the solution showed the typical fluorescence of the Ce^{3+} ion, which increased with irradiation time. A constant value was obtained when all $acac^-$ ligands were substituted by chloride ions (Fig. 2). At this point the solution was evaporated in Petri dish to obtain polymeric film, doped with cerium. The films were analyzed by emission and FTIR techniques. For the purpose of comparison, films of pure PVC were analyzed.

The emission spectra showed that the films are phosphors emitting typical fluorescence of Ce^{3+} ion in 350–370 nm range and that the matrix did not contribute to the observed luminescence. The lack of the polyene luminescence suggested that the radicals produced decay mainly by chemical quenching with the oxygen, thus the formation of the conjugate double bond and polyene formation was negligible.

FTIR spectra (Fig. 3) do not show significant changes of the relevant PVC bands. Characteristic PVC bands in the 3000–2800 cm^{-1} regions (C–H_x stretches), 1400–1300 cm^{-1} and 700–600 cm^{-1} (C–Cl stretch) remain unchanged [26]. This indicates that the very little photodehydrochlorination was enough to complete Cl^-–$acac^-$ substitution.

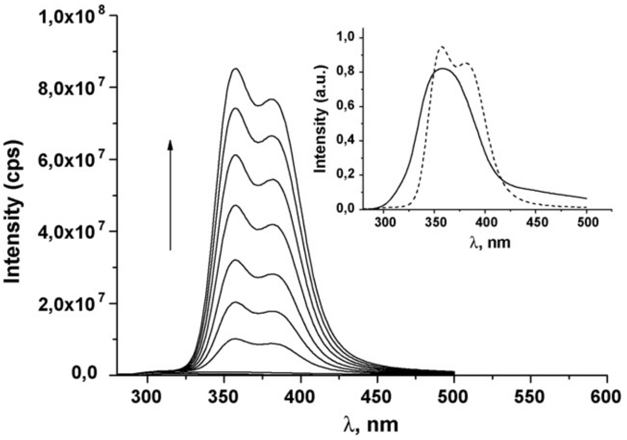

Fig. 2. Luminescence increase as a result of $CeCl_3$ formation for irradiation of THF solution 0.2 M in PVC and 10^{-4} M in cerium complex; irradiation times: 0–3 h. Inset: comparison between the emission spectrum of $CeCl_3$ obtained in THF solution containing PVC (– – –) and the emission spectrum of film obtained evaporating the same solution (—).

Note that, after irradiation carbonyl groups are evident in the 1700–1780 cm^{-1} region. These bands can be associated with photooxidation products.

The obtained results encouraged us to look for the possibility to obtain luminescent films, by synthesizing fluorescent cerium chloride *in situ*. With this aim, we carried out investigations into the irradiation of PVC films containing 0–3 cerium complex weight percentages.

The pure films of PVC absorbed about 1.5% of the incident light, and did not exhibit luminescence over 320 nm. The irradiation provoked chemical modifications whose course was followed through absorption, emission and FTIR spectrophotometry. After irradiation, the films exhibited absorption at about 280 nm which exponentially increased with irradiation time (Fig. 4), as expected for radical reactions. Luminescence emis-

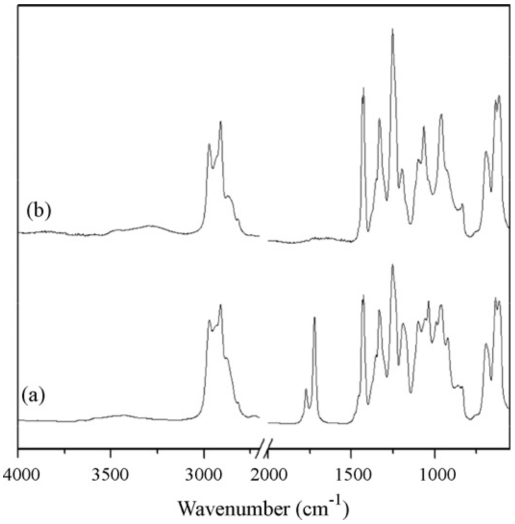

Fig. 3. FTIR spectra of (a) irradiated THF solutions containing PVC (0.2 M) and $Ce(acac)_3$ (10^{-4} M) evaporated on a Petri dish and (b) pure PVC films.

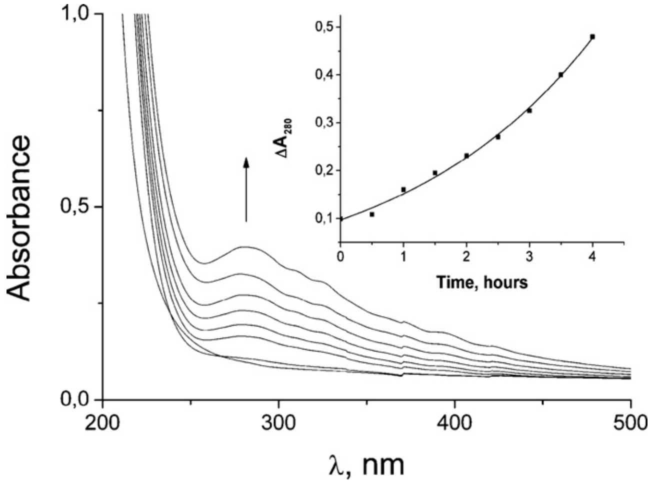

Fig. 4. The absorbance increase as a result of the irradiation of pure PVC film; irradiation times: 0–4 h. Inset: exponential increase of the band at 280 nm.

sion appeared at about 410–430 nm (Fig. 5), for excitation at 300 nm.

The typical shape of the absorption and excitation spectra (Fig. 5, inset) were consistent with the presence of polyene sequences [27], likely formed by PVC photodehydrochlorination.

The rate growth of the absorption maximum at 280 nm was consistent with the increase of the conjugated bonds. Within 3 h, in the irradiated films no insoluble gel was detected. This indicated that photocrosslinking and reticulation processes were negligible for the absorbed dose of light. For prolonged irradiation, a decrease of the luminescence was observed and after 12 h of irradiation some photocrosslinking was evaluated by the percentage of insoluble gel (about 20%).

No remarkable changes were observed in the FTIR spectra, nevertheless they provided information regarding oxidation products. The data showed that carbonyl groups in the 1700–1780 cm^{-1} region (Fig. 6) were formed at the initial irradiation, then these bands increased very slowly with irradiation time. These findings suggest that the initial formation of the oxidation products was due to some impurity or imperfection present in the film. Note, however, the presence of bands in the 3050–3150 cm^{-1} region after 240 min of irradiation which were not observed in the corresponding PVC irradiated in solution. These bands can be correlated to C–H stretches of sp^2 hybridized carbon in some cyclic configuration or very strained carbon (such as epoxides) [26]. These can be associated with the photoxidative decomposition of the PVC after a very long irradiation.

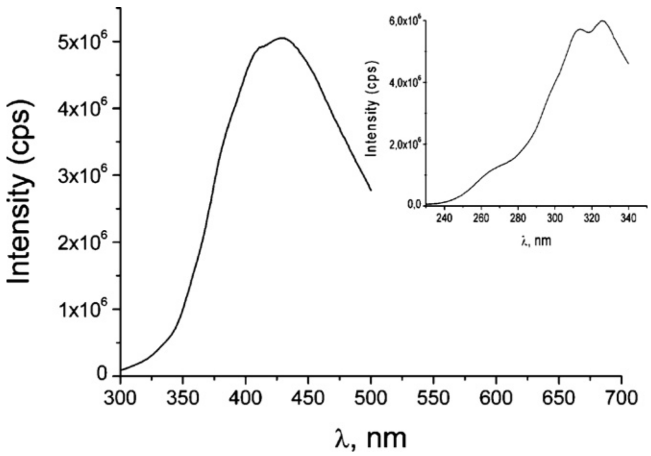

Fig. 5. Luminescence of a pure PVC film, after 3 h of irradiation at 254 nm, $\lambda_{exc} = 300$ nm. Inset: excitation spectrum, $\lambda_{em} = 410$ nm.

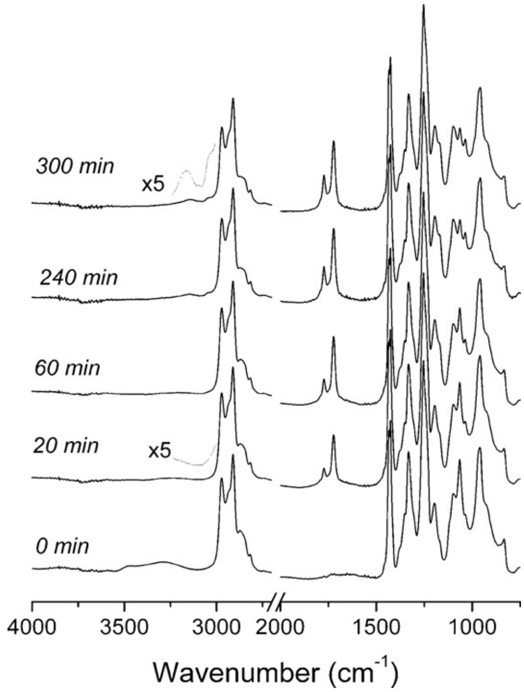

Fig. 6. FTIR spectra pure PVC films at various irradiation time.

The presence of cerium complex in the concentration range (0.1–3%) changed the absorption and luminescence properties of the films.

The optical density below 300 nm increased as the cerium complex percentage increased, and the fraction of 254 nm light, initially absorbed by PVC and cerium complex, respectively, changed in a complementary way (Fig. 7).

After irradiation, both polyene and $CeCl_3$ emissions appeared. This showed that in rigid matrix the $CeCl_3$ formation occurred by $acac^-$–Cl^- substitution like that observed in solution. Because the complex shields the incident light, it can be expected that photodehydrochlorination occurred more slowly and that the irradiation time necessary to obtain luminescent films increased with the percentage of cerium complex. Besides, note that it is possible to evidence the cerium chloride emissions when its absorption of the light at 260 nm, exciting wavelength of its fluorescence, is enough to compete with other species present (initial complex or polyenes). The experimental results confirmed that which was expected. For example, the photochemical behaviour for two films, containing, respectively 0.1% and 1% of cerium complex are reported in Figs. 8–11.

For films containing 0.1% of complex, the incident light was equally shared between the complex and the PVC which absorbs about the same light as it does in the absence of complex. For irra-

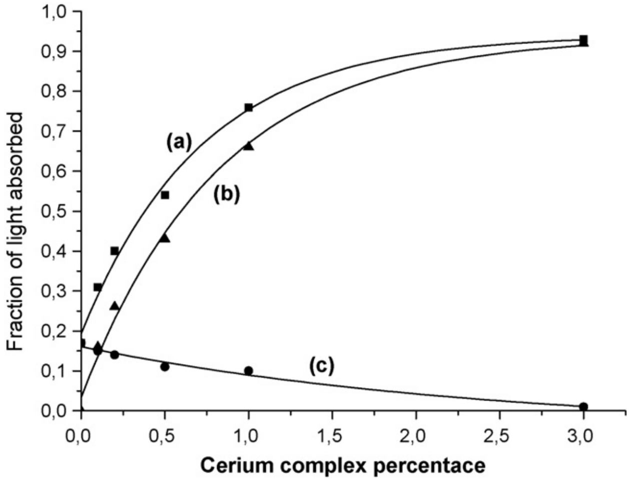

Fig. 7. Light absorbed variations ($t = 0$ min) as a result of the increase of the cerium complex percentage for (a) the film, (b) the cerium complex and (c) the PVC.

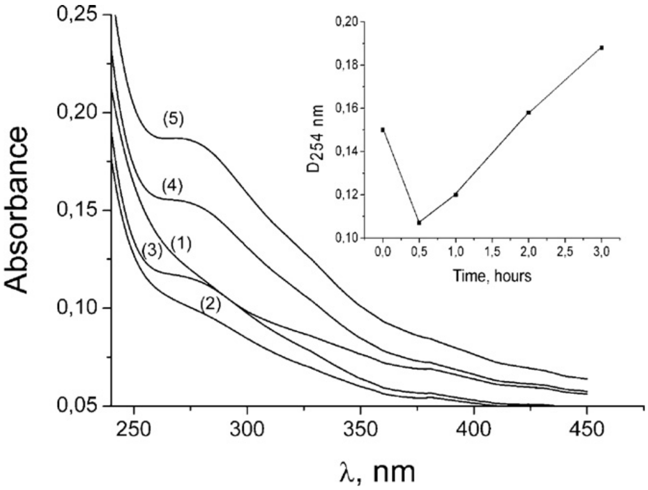

Fig. 8. Spectral changes of PVC film, containing 0.1% of complex, irradiation times: (1) 0′, (2) 30′, (3) 60′, (4) 120′ and (5) 180′. Inset: absorbance chances at 254 nm vs. irradiation times.

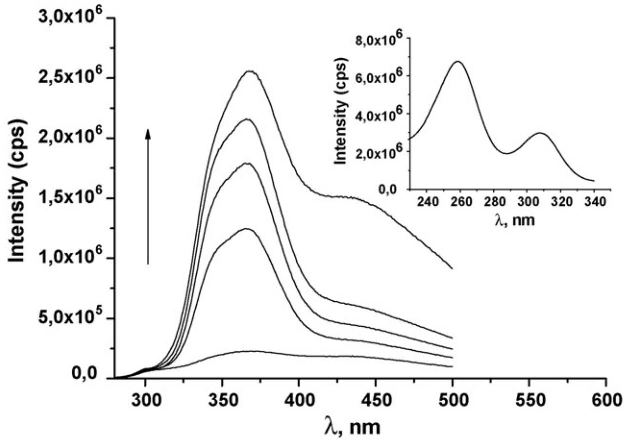

Fig. 9. Luminescence increase of a PVC film containing 0.1% of Ce(acac)$_3$; irradiation times: 15–180 min and $\lambda_{exc} = 260$ nm. Inset: excitation spectrum registered after 30′ of irradiation, $\lambda_{emiss} = 350$ nm.

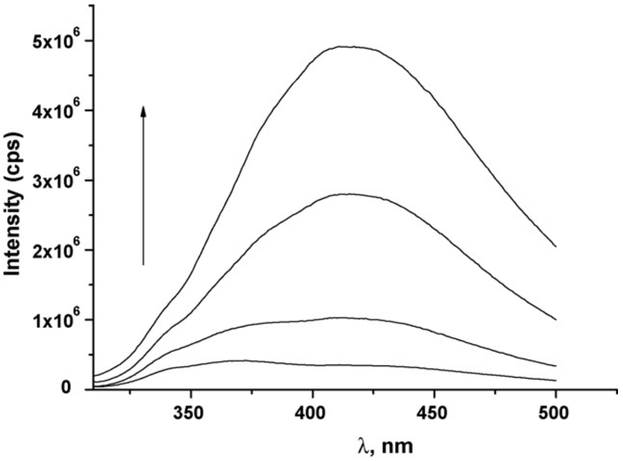

Fig. 10. Luminescence increase of a PVC film containing 0.1% of Ce(acac)$_3$, $\lambda_{exc} = 300$ nm; irradiation times: 15–180 min.

diation, initially the absorption spectrum decreased, due to the decomposition of the complex, as found in Ce(acac)$_3$ solution photochemistry, but successively it increased, due to polyene formation with a maximum at about 280 nm (Fig. 8).

For short irradiation times, the film emitted both the luminescences of the cerium and that of the polyenes, evidenced well for excitation at 260 and 300 nm, respectively (Figs. 9 and 10). Both emitting species contributed to luminescence spectrum at excitation wavelengths of 260 nm. From deconvolution of the bands in Fig. 9, it was found that the CeCl$_3$ fluorescence continued to increase until about 1 h of irradiation and successively remained constant, whereas the PVC luminescence exponentially increased. In these conditions the fluorescence quantum yield of CeCl$_3$ was calculated. The found value was 0.5 ± 0.05.

In the film containing 1% of cerium, 86% of the incident light was absorbed by the initial complex. For irradiation, the UV spectrum decreased and after a period (about 70 min), the cerium and PVC emissions started to appear (Fig. 11) and increased with the irradiation time. In these conditions, the fluorescence of the cerium is about ten times higher than in the previously

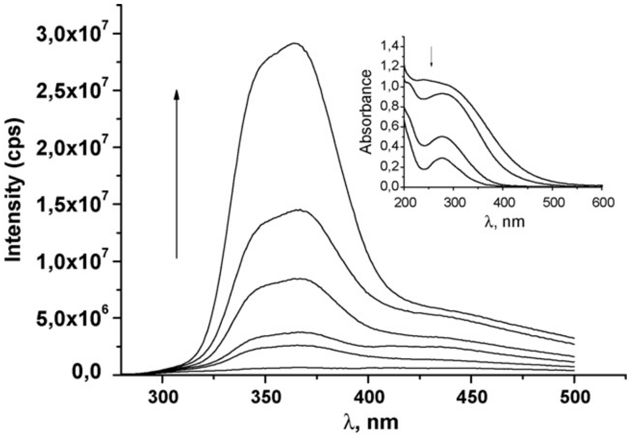

Fig. 11. Luminescence of PVC film containing 1% of Ce(acac)$_3$ irradiated at various times, $\lambda_{exc} = 260$ nm; irradiation times: 0–3 h. Inset: absorbance spectral changes of the same film irradiated for 0, 1, 2, 3 h.

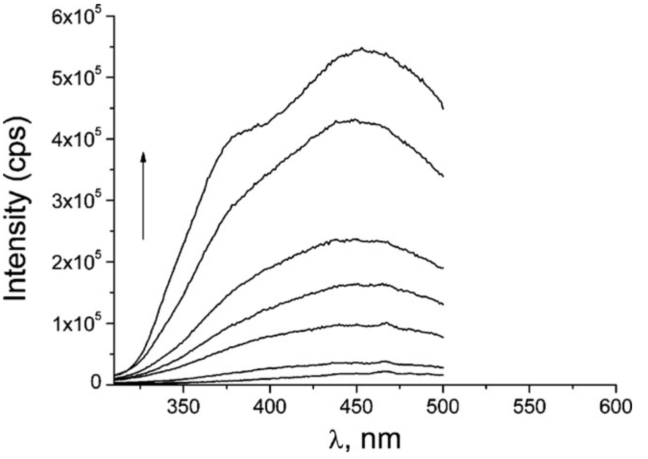

Fig. 12. Luminescence variation as result of the irradiation of a film di PVC containing 3% of Ce(acac)$_3$, $\lambda_{exc} = 260$; irradiation times: 0–3 h.

considered films, whereas the PVC luminescence attained the same value.

For films with 3% of cerium (Fig. 12), the time necessary to observe cerium fluorescence is longer than that for PVC, thus the first appeared as a shoulder in the luminescence band of the polyenes.

In all films, the cerium fluorescence attained a maximum value, then it was decreased and was overlapped by polyene luminescence.

The FTIR spectra showed that the presence of cerium complex in the films does not change the chemical course of the PVC photodegradation since the spectra are similar to the corresponding spectra of pure PVC.

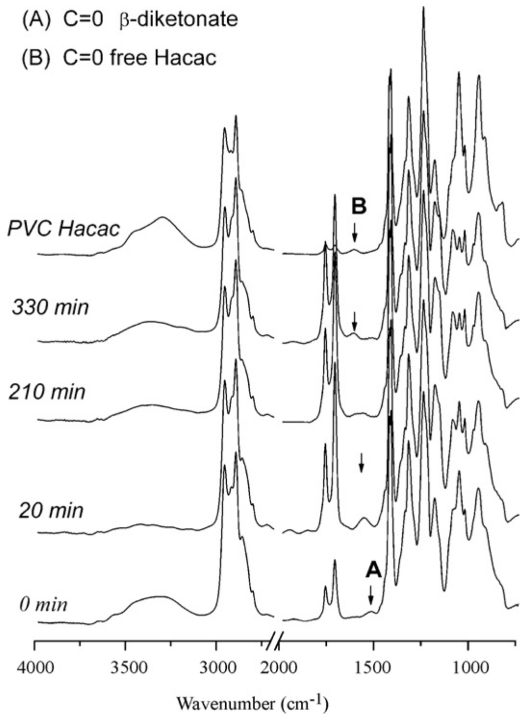

Fig. 13. FTIR spectra of 3% Ce(acac)$_3$ containing PVC films at various irradiation times. For comparison, FTIR spectra of free Hacac in a PVC film has been added on the top.

In addition FTIR spectra of PVC films containing 3% Ce(acac)$_3$ (Fig. 13) show the typical band in the 1600–1500 cm^{-1} region due to β-diketones coordinated to metals [28]. However, the shape and position of this feature, a single

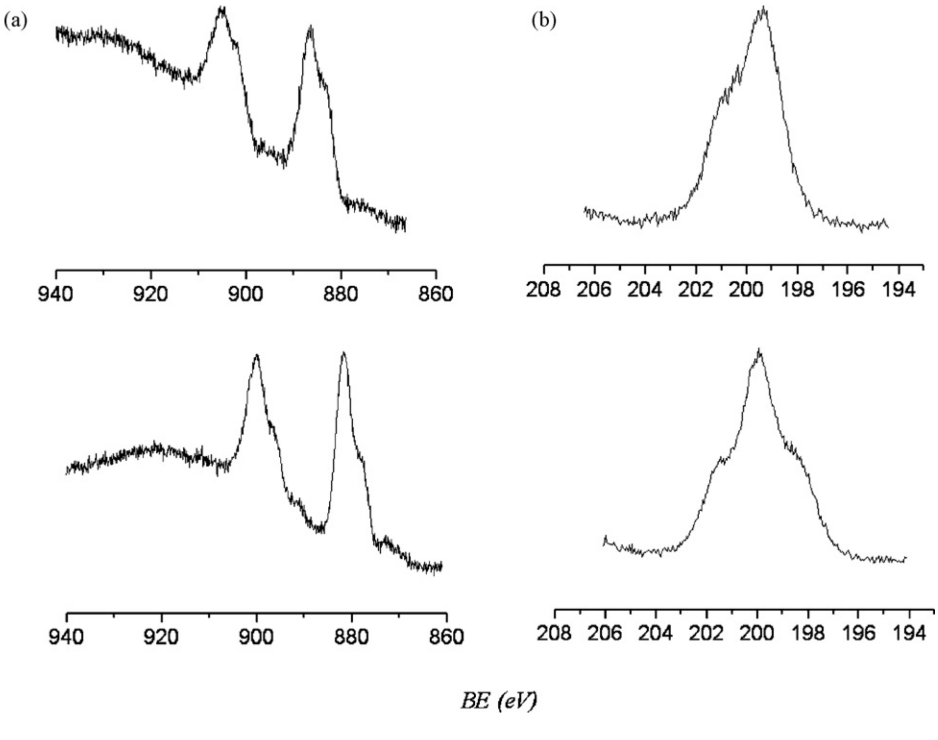

Fig. 14. High resolution XPS spectra in the relevant regions of binding energy (BE) for Ce doped PVC films before (above) and after (below) irradiation. (a) Ce 3d and (b) Cl 2p.

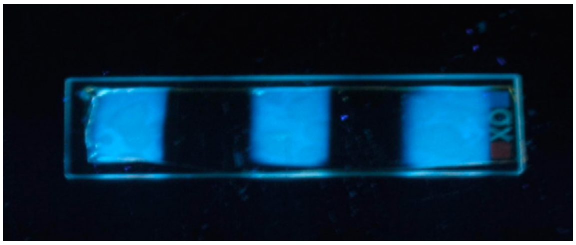

Fig. 15. Photograph of a patterned film (1 cm × 3 cm) of PVC containing 1% of $Ce(acac)_3$ on a quartz substrate irradiated for 1 h. The experiment was performed using a photomask to shadow the substrate during the irradiation.

band centred at 1534 cm^{-1}, is different from the doublet at 1590 and 1514 cm^{-1} of $Ce(acac)_3$ powders. These findings agree with the above mentioned UV observations and point to a different rearrangement of the coordination sphere of the complex in PVC which acts as an aprotic solvent.

As the photoreaction is occurring, the band shift towards higher wave numbers, indicating that the complex undergoes some rearrangement. After a long irradiation time (330 min), a feature at 1620 cm^{-1} is evident which is due to the presence of free Hacac in the PVC. The presence of this band confirms that the $acac^-$ ligand is substituted by Cl^-, provided from the photo produced HCl, with the consequent formation of free ligand.

Finally the nature of the photoproduct in the PVC film was investigated by XPS analysis. High resolution XPS spectra in the relevant regions of binding energy (BE), namely Ce 3d and Cl 2p, are shown in Fig. 14 for Ce doped PVC films, before and after irradiation. In both films the Ce 3d feature (Fig. 14 (a)) shows a complex structure consisting of a main Ce $3d_{5/2}$–Ce $3d_{3/2}$ spin-orbit doublet (around 886.6 and 905.4 eV, respectively). These BEs are consistent with the presence of Ce^{3+} ion and due to either $Ce(acac)_3$ or $CeCl_3$ [28] compounds. Note that each Ce 3d spin-orbit component consists of two features: the higher peak is due to a ground state (GS) $3d_{5/2}$–$3d_{3/2}$ photoemission and the lower BE shoulder is due to a charge transfer (CT) photoemission [29,30].

More evident changes due to irradiation can be observed in the Cl 2p spectral region (Fig. 14 (b)). In particular, before irradiation the BE values of the Cl $2p_{3/2-1/2}$ spin-orbit doublet ($2p_{3/2}$ 199.3 and $2p_{1/2}$ 200.9 eV) are consistent with the Chlorine bonded to carbon atoms in PVC (Cl^{PVC}). After irradiation a shoulder become evident at low BE due to the presence of inorganic chlorine. The Cl 2p feature can, therefore, be fitted with two doublets: the first doublet due to Cl^{PVC} and a second component Cl^- at 198.7 and 200.4 eV which is consistent with the presence of $CeCl_3$. Note, in addition, that the Cl^-/Ce atomic ratio calculated from XPS spectra is about three, as expected.

The film irradiation performed by using a mask resulted in direct photopatterning. The luminescence emission occurred exclusively from directly irradiated zones, thus no reaction occurred for the migration of reactive species. In Fig. 15 a patterned PVC film containing 1% of cerium complex, after 60 min of irradiation, is reported.

It is noteworthy that SEM analysis of the films, before and after irradiation, did not show significant change of the morphology or crack formation.

4. Conclusions

The overall results suggest some interesting considerations regarding the photochemical synthesis of the photoluminescent PVC, doped with Ce^{3+} ion. It is noteworthy to observe that the photochemical behaviour of the studied complex shows the same mechanism in both liquid solution and in rigid matrix, involving the formation of HCl, the ligand substitution and its successive degradation. These findings indicate that the $Ce(acac)_3$ was dispersed in PVC and no chemical bond with the polymer was present and this is consistent with the lack of complex influence on PVC degradability.

The work confirmed the versatility of the photochemical method in the synthesis of materials with specific characteristic through a simple and low cost procedure, using raw materials which are easily available on the market. In brief we provided PVC with an important property, luminescence, without damaging it. Unlike earlier procedures proposed, we used a starting compound soluble in a solvent suitable to prepare films and no complicated operation was necessary. Besides this, because no migration of reactive species occurred in rigid matrix, the photochemical event was limited to around the point that the light hit directly. As a consequence, the preparation *in situ* of the fluorescent cerium allowed us to obtain a patterned fluorescence. In fact, by irradiating film through a mask with a suitable design, patterned fluorescent figures can be obtained. Besides, figures with a variable intensity of fluorescence can be prepared, by modulating the light dose, whereas emissions at different intensities and wavelengths can be achieved by selecting the suitable excitation wavelength. The above experiments suggest that the films containing cerium complex 1% w/w provide better results regarding the possibility of obtaining luminescent material without damaging side effects to the matrix.

The proposed method can be further explored to test the direct photo writing of luminescence pattern, using mixtures of lanthanide complexes which permit the tuning of the emission wavelength by choosing suitable chemical compositions and excitation wavelengths.

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