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Study of secondary relaxations in poly(vinyl chloride) by phosphorescence decay Effect of the chemical structure and the concentration of luminescent probes

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Abstract

The phosphorescence emission of both naphthalene and pyridine can be used to detect the secondary (β) relaxation of PVC, as this relaxation manifests by a decrease in the emission from the grafted probe at the temperatures at which the local motion at the backbone begins. In this work, an extensive study of the kinetic and spectral features of the phosphorescence of 4-mercaptopyridine, 4-methoxybenzenethiol and 4-mercaptophenol groups as a function of temperature is presented. These three luminescent probes have been grafted onto PVC, with modification levels ranging from 3% up to 46%. The phosphorescence decay from −130 °C up to 30 °C has been followed and both the intensity of the emission and the spectral features have been studied as a function of temperature. The interaction between probes as the concentration increases leads in all cases to the emission from aggregates or excimers, which have features different to those of the isolated probe. Side reactions occur when grafting the hydroxyl containing probe, what also leads to surprising phosphorescence spectral and decay rate features.

Keywords: Poly(vinyl chloride); Phosphorescence; Secondary relaxation; Grafting

1. Introduction

One of the main difficulties in the understanding of the structure of substances without long range order and out-of-equilibrium thermodynamics is the impossibility to infer local structure from macroscopic properties. This is the case of glassy solids and in particular of polymers below their glass transition temperature. Properties such as mechanical and dielectric characteristics and behaviours such as physical aging depend dramatically on this point, what makes the relevance of this circumstance both academic and practical.

The search for characterization tools able to probe the local structure of glassy polymers is thus of great importance. Among the candidates for such studies, the marking techniques ^{13}C NMR or neutron scattering using labelled and unlabelled chains are well known [1,2]. The inclusion, either by impregnation or by grafting, of luminescent probes has also being explored in the last decade, and several authors have studied secondary relaxations of homopolymers, copolymers and blends by means of luminescent probes, which were incorporated, free or covalently attached, to the polymer matrix [3–6]. One of many attractive characteristics of luminescence is the large number of available probes with a wide variety of shapes, sizes, and photophysical properties that depend on the nature of the environment in which they are incorporated and the range of temperatures studied. The emission of the luminescent guest is sensitive to the relaxation processes related to the polymer matrix, since the emission of the molecular luminescent probe depends on both its intrinsic photophysical properties and the interactions developed with the surrounding polymer matrix. In general, a decrease in lumines-

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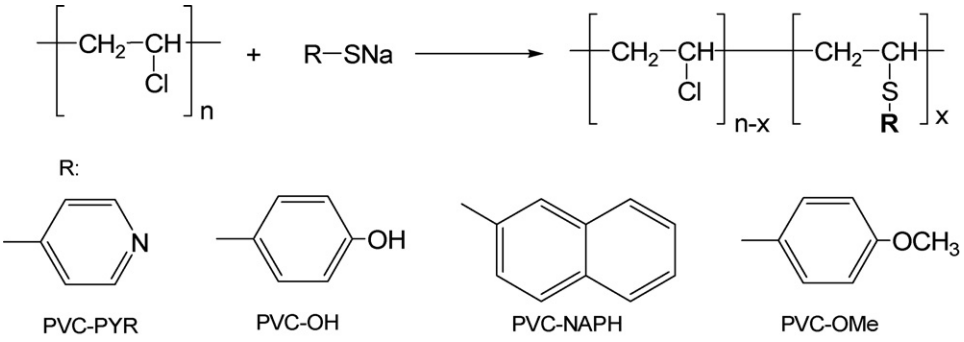


Scheme 1.

cence intensity with the temperature increase is observed, and it is theorized that enhancement of the free volume of the medium leads to an increase in the non-radiative decay rate and consequently a decrease in luminescence quantum yield. For instance, the temperature dependence of the long-lived phosphorescent state has been useful to determine local motions at lower temperatures, while the short lived fluorescent state has been more useful to monitor processes taking place at higher temperatures.

The advantages of such approaches with respect to conventional techniques are many-fold: high sensitivity and selectivity, very short time response (down to 10^{-9} s) and its non-destructive character. However, the interpretation of the results is not straightforward because the introduction of a medium size molecule or chemical group in the polymer obviously alters the local structure of the site at which grafting takes place, i.e., precisely at the site which will be studied by the probe [7].

In a recent paper [7] we showed how the kinetics of the phosphorescence decay of two different luminescent probes grafted onto the polyvinyl chloride (PVC) backbone changes on approaching a local motion of the PVC backbone, known as β relaxation, which takes place at temperatures about −60 °C. Though the detection of the motion was clear with both probes, several specific features led open the possibility that the local phenomena visualized in each case could be different in a subtle way. The most outstanding feature was the fact that the smallest probe (pyridine) provides more information than the largest one (naphthalene), since the size of the polymer segments involved in the relaxation process which contributes to the enhancement of free volume, must be larger than the size of the probe to produce a significant change of the probe photophysical properties. The phosphorescence analysis of pyridine as a function of temperature seemed to indicate that contiguous modified segments which interact with one another do not relax, while isolated modified segments do relax, either because isolated modified segments display the motions characteristic of the relaxation or because they are sensitive to the motions of contiguous unmodified PVC segments. It was shown that a solid knowledge on the grafting procedure and characteristics is needed if a correct interpretation of the results is to be made. In this work we extend the study to other two probes, and discuss not only the kinetics of the decay but also the spectral features of each chromophore, which, because of their specific chemical features, lead to very different results.

2. Experimental

2.1. Materials

Commercial bulk polymerized PVC with a weight average molecular weight M_W of 58.000 g/mol was obtained from ATOCHEM, Spain. The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

2.1.1. Modification of PVC

0.5 g (8 mmol) of PVC and 8 mmol of sodium salts of 4-mercaptopyridine and 4-methoxybenzenethiol, respectively, obtained by reaction with sodium hydride according to a procedure described elsewhere [8] were dissolved in 50 ml of cyclohexanone and the reaction started under N_2-atmosphere at 60 °C. In the case of PVC modification with 4-mercaptophenol, the salt was formed in situ using 12 mmol of sodiumcarbonate.

The reactions were stopped by precipitation of the mixture in cold methanol/water (2:1). The modified polymers were purified using THF/methanol (for samples with a degree of modification of less than 20%) or THF/hexane (for higher modification degree) as a solvent–precipitant system. The structure of modifiers and copolymers used in this work are depicted in Scheme 1. The grafting percentage was determined using ^{1}H-NMR spectroscopy. The polymers modified with 4-mercaptopyridine, 4-methoxybenzenethiol and 4-mercaptophenol will be called hereafter PVC-PYR-X, PVC-OMe-X and PVC-OH-X, respectively, where X denotes the modification degree. A detailed sample description is given in Table 1. Films were prepared

Table 1
Physicochemical characterization of the PVC and the studied copolymers

Name	Modifier	% grafting	Thickness (μm) ± 3
PVC	None	–	50
PVC-OMe-7.3	4-Methoxybenzenethiol	7.3	43
PVC-OMe-46.3	4-Methoxybenzenethiol	46.3	15
PVC-OH-3.0	4-Mercaptophenol	3.0	47
PVC-OH-9.9	4-Mercaptophenol	9.9	70
PVC-OH-21.7	4-Mercaptophenol	21.7	35
PVC-PYR-9.7	4-Mercaptopyridine	9.7	42
PVC-PYR-26.3	4-Mercaptopyridine	26.3	60
PVC-PYR-31.4	4-Mercaptopyridine	31.4	53
PVC-PYR-43.1	4-Mercaptopyridine	43.1	55

by casting of THF solutions and subsequent drying or by compression moulding at 140 °C for 3 min.

2.2. Photoluminescence measurements

Probes were characterized in solution using various solvents and concentrations. UV absorption spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Fluorescence and phosphorescence emission spectra of solutions were obtained using a Perkin-Elmer LS-50B luminescence spectrophotometer, and corrected by means of the response curve of the photomultiplier.

Photoluminescence measurements on samples in film form were realised using a homemade apparatus as described elsewhere [9]. The analysis range was [220–840 nm] and the resolution was 4.5 nm. Phosphorescence lifetime estimation was made by means of a photomultiplier working in photon counting mode. Using a thermally regulated sample holder, we achieved measurements in the temperature range [−130 °C, 45 °C]. All photoluminescence measurements were made in Helium atmosphere at atmospheric pressure. Spectra were acquired along continuous excitation or at excitation switch off with CCD acquisition synchronized by closure of the excitation shutter. All spectra are represented as normalized spectra. Quantitative information is provided in intensity versus temperature plots.

2.3. Physical and chemical characterization of the copolymers

2.3.1. Microstructure

The chemical composition distributions of PVC modified with sodium thiophenolate, PVC-OMe-X, PVC-OH-X and PVC-PYR-X copolymers have been studied by ^{1}H and ^{13}C NMR spectroscopy on a 300 MHz XL Varian spectrometer in deuterated nitrobenzene under standard conditions at 90 °C, finding that the resulting microstructure is as in other thoroughly studied cases [10].

2.3.2. Mechanical relaxations

The dynamic mechanical analysis (DMTA) spectra of some of the samples (see Table 1) were registered by using a Thermal Instrument DMA 983 analyser in flexion mode from rectangular strips of 6 mm × 4 mm × 0.4 mm in dimension obtained by compression moulding. The temperature dependence of the loss modulus was determined at 0.1 Hz, between −130 °C and 100 °C, at a heating rate of 5 °C min^{-1} and using a deformation amplitude of 0.8 mm.

2.3.3. ATR-FTIR

The spectra were recorded on the membranes using a FTIR Perkin-Elmer Spectrum-One, 10 scans and 2 cm^{-1} resolution.

2.3.4. SEC analysis

The molecular weight analysis of some synthesised copolymers was performed by means of size-exclusion chromatography using a Waters 1515 HPLC pump, Waters 2414 refractive index detector, and a set of three Waters columns with nominal pore sizes of 10^2, 10^4, and 10^6 Å. The eluent was THF at 35 °C, pumped at 1 mL min^{-1}.

More details on the physicochemical characterization can be found in previous work on these copolymers [11].

3. Results and Discussion

3.1. Dynamic mechanical analysis

Results for the mechanical loss modulus as a function of temperature of neat PVC appear in Fig. 1, together with those related to PVC-OMe-5.3, PVC-OMe-36, PVC-OH-11.9 and PVC-PYR-6. The progressive substitution of chlorine atoms leads to the gradual decrease of the β relaxation intensity. This decrease mostly takes place at the high temperature side of the relaxation, so that it brings about a shift to low temperature of the maximum of the loss tangent or loss modulus, as shown in Fig. 1. The sample in which a 36% of the Cl atoms have been substituted by 4-methoxybenzenethiol groups (PVC-OMe) has in fact no β relaxation at all. This copolymer has a double α relaxation (associated to T_g), one at the same temperature as PVC (90 °C), and a second at 70 °C, which is also seen as a shoulder in PVC.

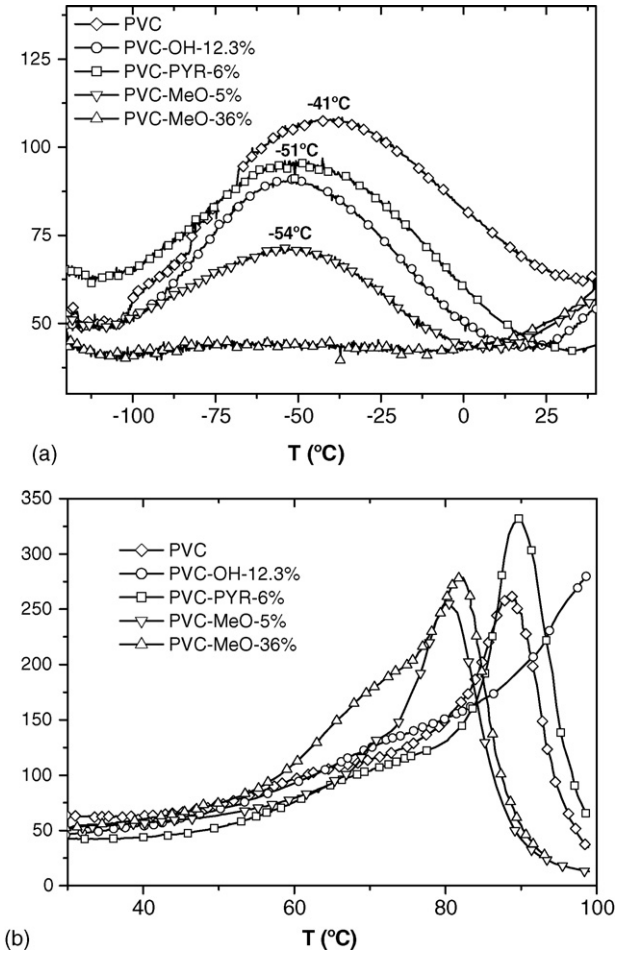


Fig. 1. Mechanical loss modulus as a function of temperature for PVC, PVC-OH-12.3, PVC-PYR-6, PVC-OMe-5 and PVC-OMe-36. Stress frequency = 0.1 Hz: (a) β-relaxation region; (b) α-relaxation region.

The effect of Cl substitution on the β relaxation is qualitatively the same, regardless of the type of substituent. In contrast, the α relaxation depends on the chemical structure of the nucleophile. As seen in Fig. 1b, and consistently with previous work [12], when substituents are bulky or able to interact strongly with one another, as is the case of PVC-OH, T_g increases, when substituents are not able to interact as is the case of PVC-OMe, it decreases.

Before a 36% of modification is reached, β relaxation completely disappears. This, together with the fact that different types of nucleophiles produce the same effect on it proves once more the local nature of the relaxation and the fact that with about a 70% of the chlorine atoms still present, the relaxation no longer exists. This can be due either to the connection of this local motion with not all, but a fraction of Cl atoms, what has been discussed in a number of articles [13], or to the minimum segment length necessary for the motion to take place.

In a former work, the use of certain nucleophiles as phosphorescence probes allowing the local study of the motions in their environment was proposed. 4-Mercaptopyridine, in particular, proved to be very useful in the study of the β motion of PVC. When studying the β motion by DMTA at 0.1 Hz, only a broad envelope peaking at −41 °C can be seen. However, when monitoring the same relaxation by phosphorescence decay it appeared that it is constituted by two components, one at about −60 °C and the other at about −40 °C [7]. In fact, the shift towards lower temperatures depicted in Fig. 1 is caused by the disappearance of the high temperature component, rather than by an actual shift of the relaxation to lower temperatures. In this sense, phosphorescence decay rate proved to be more sensitive than DMTA for probing overlapping relaxation processes.

However, the study of relaxation mechanisms from the standpoint of phosphorescence quantum yield and lifetime inevitably leads to the problem of the equivalent frequency since the observed temperature for a relaxation depends on the frequency used to probe it. One of the reasons for variations in the phosphorescence lifetime and quantum yield is linked to the competition between radiative and non-radiative deactivation paths of a triplet excited state. An increase in temperature favours the interactions with nearby environment leading to a decrease in yield and a decrease in the apparent lifetime. It was considered that if phosphorescence is quenched by a process somehow linked to a relaxation, this process must happen within a time corresponding to the lifetime, providing so an answer to the problem of equivalent frequency. As for phosphorescence the lifetime ranges from 1 ms to 10 s, the equivalent frequency comes into the range 0.1 Hz to 1 kHz. However, it has been observed [3–6] that in other polymers the secondary relaxations can be detected by using fluorescent probes at temperature ranges close to those detected by DMTA. Following the above scheme, for fluorescence the equivalent frequency would be in the range of GHz, which appears not consistent with the observations. The feeling of many researchers is that the luminescence yield is controlled by the increase in free volume and hence, for the equivalent frequency it is more appropriate to think in terms of equivalent frequencies estimated in temperature ramp experiments; of the order of 0.01–0.1 Hz, considering for instance the equivalence between DMA and DSC when measuring the T_g, or the equivalence between dynamic experiments (either mechanical or dielectric) and thermostimulated techniques.

Two probes of different structure were studied in the previous work: 4-mercaptopyridine and 2-mercaptonaphthalene [7]. The different behaviours of the two probes evidenced one of the characteristics of this type of study: the local nature of the information provided by each probe. Though most probably the strong change in phosphorescence decay rate seen in the range −80 °C to −30 °C is related to the PVC β-relaxation, both the intensity of the relaxation, the number of components and the actual temperature position of each of them depends on some or all of the following: (i) grafting reaction stereochemistry, (ii) local structure modifications introduced by the graft itself (local free volume and stiffness), (iii) extent of the reaction (%) and (iv) nature of the probe itself. The first three points were discussed in the referred work. In what follows, an exhaustive study of the phosphorescence intensity and spectral features is performed for probes with different chemical structures, in the temperature range from −130 °C to 30 °C.

3.2. Phosphorescence decay

3.2.1. Phosphorescence decay as a function of temperature

In the preceding work, 4-mercaptopyridine was chosen as probe because it is the one with the simplest luminescent behaviour; 2-mercaptonaphthalene, which is bulkier, does not strongly differ from 4-mercaptopyridine as regards luminescent decay kinetics. Fig. 2 completes the information already published [7] and draws a much more complicated panorama.

Once the features of the PVC-PYR phosphorescence decay with temperature are understood (those depicted on the right-hand side of Fig. 2) it is possible to understand the information provided by probes with different chemical features. The phosphorescence decay rate of PVC-PYR changes on reaching the temperature region of −60 °C to −40 °C, and this is so because in that temperature interval PVC undergoes its β relaxation, with the subsequent increase in local mobility and in the radiationless deactivation probability of excited electronic states.

The left-hand side of the figure shows the phosphorescence decay of the three other probes studied in this work. PVC-NAPH (PVC modified with 2-naphtalenethiol) exhibits a behaviour similar to PVC-PYR up to a 7% modification, posing no special difficulty. Over an 8% or 9%, the nucleophilic substitution of chlorine atoms by the very bulky 2-naphtalenethiol is quite difficult and has not been done, so no information on the behaviour at high modification degrees is available at the moment. PVC-OH and PVC-OMe however, behave in quite a different fashion. In the absence of the DMTA analysis shown in the preceding section, it could be suspected that the introduction of these two probes creates another relaxation in PVC at much lower temperature (<−100 °C). But this is not the case, since at least no mechanically active relaxation is detected, and consequently the quick decay shown in Fig. 2 must be related to a relaxation involving the probe itself.

In PVC-OMe, the low temperature decay is so strong that the β relaxation can be just suspected if its actual position is known.

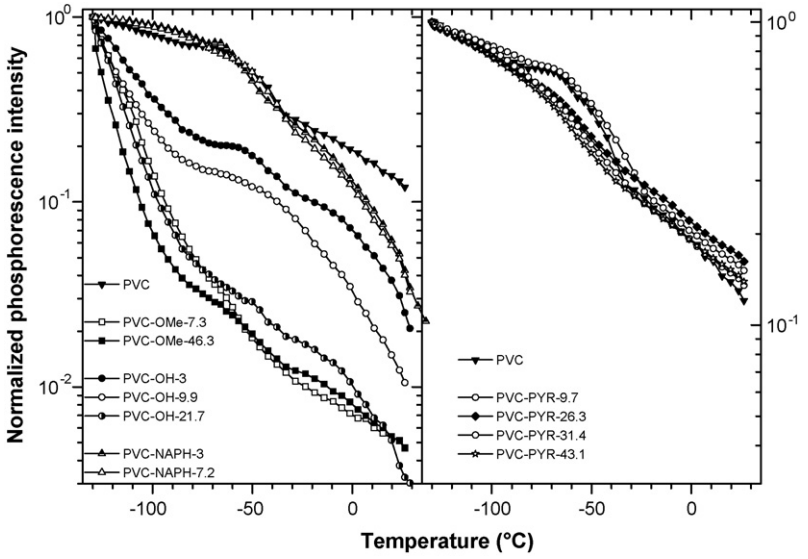


Fig. 2. Phosphorescence decay as a function of temperature for all the phosphorescent probes studied. The intensity was normalized to unity at −130 °C. Excitation wavelength = 280 nm. PVC-NAPH refers to mercaptonaphthalene modified PVC.

PVC-OH shows an intermediate behaviour: it certainly suffers strong deactivation from the lowest temperature recorded but the phosphorescence intensity at about −80 °C is still large enough as to allow the clear detection of the β relaxation, especially in the less modified sample. At this point it must be remembered that nucleophilic substitution of chlorine by these probes reduces the β relaxation in a dramatic way, as seen in DMTA, so it is not surprising that highly modified samples show little or no manifestation of β relaxation in phosphorescence analysis, as shown for pyridine. As both of the probes containing side groups deactivate at very low temperature, it seems likely that this deactivation is connected to motions of the side group, for example its rotation, responsible by an additional pathway for the quenching processes.

3.2.2. Phosphorescence decay rate and spectra of PVC-PYR: an aromatic probe without side group and capable of forming aggregates

Fig. 3 shows the overall intensity and the spectra as a function of temperature of a sample PVC-PYR- 9.7. Thorough analysis of this probe has been already published [7]. The β relaxation is conspicuous when monitoring the phosphorescence decay using grafted 4-mercaptopyridine as luminescent probe. Two phosphorescence bands have been identified in this material, peaking at 440 nm and in the range 485–510 nm, depending on temperature. In Fig. 3a, a higher decay rate is observed in the region −70 °C to −30 °C, corresponding to the β relaxation. Furthermore, the decay of the component at 440 nm is faster than that of the component at 485–510 nm. The double emission (at 440 nm and 485 nm) is due to the existence of isolated probes (440 nm) and of probes forming aggregates (486 nm) [14], but not excimers. The assessed formation of aggregates is supported by the fact that the PVC-PYR is difficult to dissolve in tetrahydrofuran because it forms a gel.

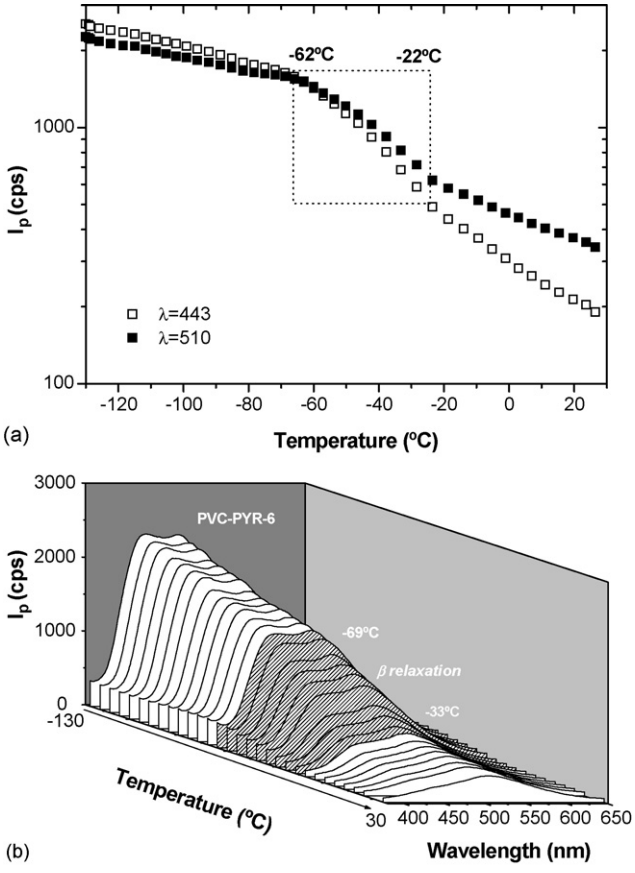


Fig. 3. (a) Phosphorescence decay of PVC-PYR-9.7 as a function of temperature monitored at 443 nm and at 510 nm. (b) Spectral evolution of PVC-PYR-9.7 (cps stands for detector counts per second).

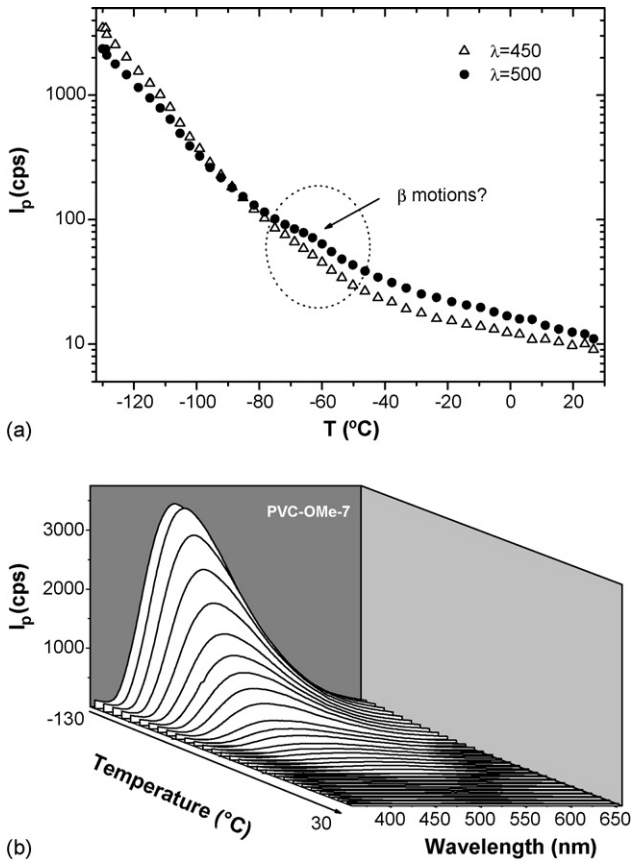


Fig. 4. (a) Phosphorescence decay of sample PVC-OMe-7.3 as a function of temperature, monitored at 450 nm 500 nm; (b) spectral evolution.

3.2.3. Phosphorescence decay rate and spectra of PVC-OMe: an aromatic probe with a side group and able to form excimers

Fig. 4 shows the results obtained for PVC-OMe-7.3. The initial phosphorescence intensity is comparable to that of pyridine base probes, and higher than phenol based ones, for this and the other PVC-OMe sample (46.3%). However, no clear β relaxation can be detected, as the probes are almost completely deactivated by −80 °C. Contrary to PVC-PYR, a single emission is seen, which can be the envelope of several components. In this connection it is noteworthy that as modification increases (from 7% to 46%) the phosphorescence peak shifts from 450 nm to 473 nm at −130 °C, while for both modification degrees the peak is at 490 nm at temperatures above −80 °C (Fig. 5).

As proposed before, the reason why the PVC-OMe system deactivates readily before −80 °C while PVC-PYR shows phosphorescence up to room temperature could be related to the rotation in the former of the methoxy side group.

In the literature it has been shown that two different phosphorescent emissions exist for polystyrene [15], one caused by oxidation of the chain, the other a broad, unstructured emission near 460 nm which has been attributed to excimers formed by two phenyl units, being not necessarily nearest neighbours [16]. By comparison with PVC-PYR results, and those found in the literature for polystyrene, we suggest that the low wavelength emission (450 nm), of the PVC-OMe family, analogous to that shown by PVC-PYR, originates at isolated probes, while the high wavelength one (490 nm) corresponds to excimers formed by nearby chromophores. It must be noted that the PVC-OMe family dissolves readily in tetrahydrofuran, even when the modification degree is 36%. Apparently no aggregates are formed, contrary to the case of the PVC-PYR family.

The chemical structure of pyridine (as well as that of the forthcoming phenol-based probe), allows significant physical interactions between grafted probes when they are sufficiently close together. The formation of these probe aggregates alters the properties of the co-polymer, for example, it modifies its behaviour in solution as shown in the preceding sections. Other properties which can be strongly modified by the presence of probe aggregates are those related to chain stiffness or to free volume. On the contrary, excimers being dimeric species which are only stable in the electronic excited state, are very interesting from a photophysical and photochemical viewpoint, but they are not however expected to affect the properties of the copolymer as much as aggregates do.

3.2.4. Phosphorescence decay rate and spectra of PVC-OH: an aromatic probe with a side group and able to form hydrogen bonds

The behaviour of PVC-OH is more complex than that of PVC-PYR and PVC-OMe. Figs. 6–9 show the phosphorescence decay as a function of temperature and its spectral evolution.

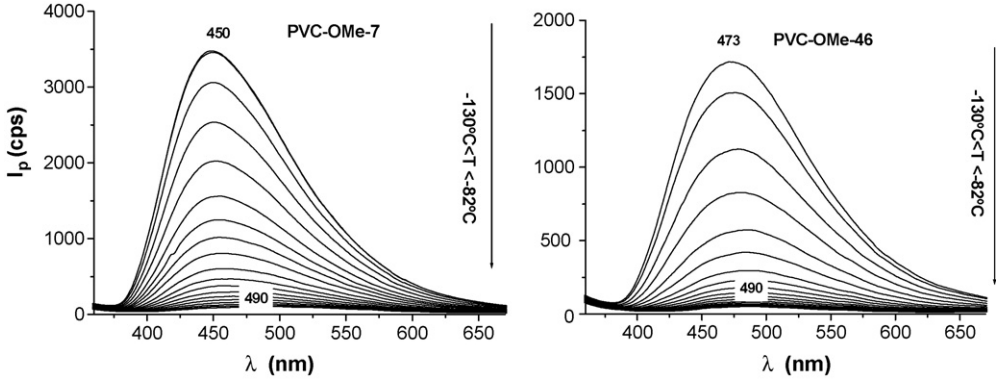


Fig. 5. Phosphorescence spectra of PVC-OMe-7.3 and PVC-OMe-46.3 as a function of temperature.

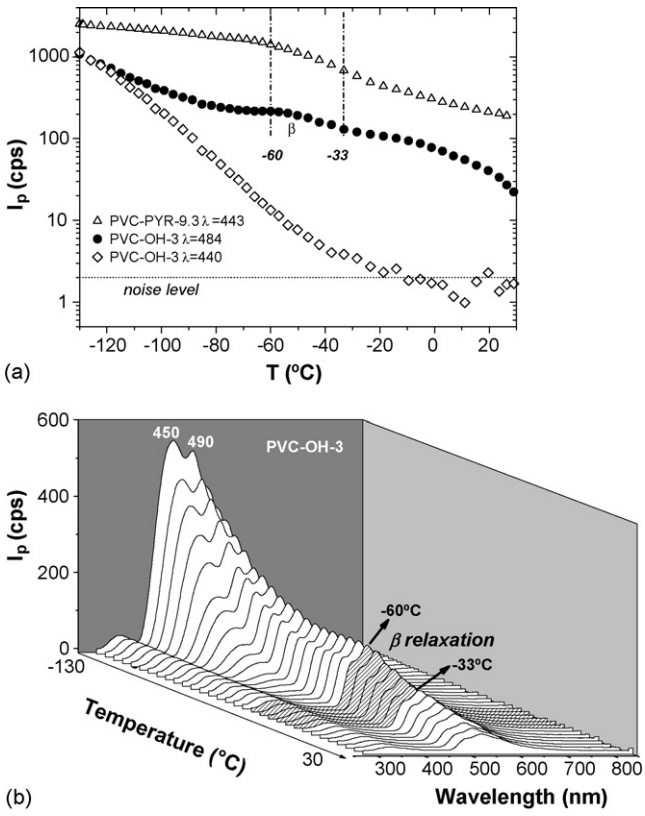


Fig. 6. (a) Phosphorescence decay of sample PVC-OH-3 as a function of temperature, as monitored at 440 nm and 484 nm compared to results for PVC-PYR-9.3; (b) spectral evolution.

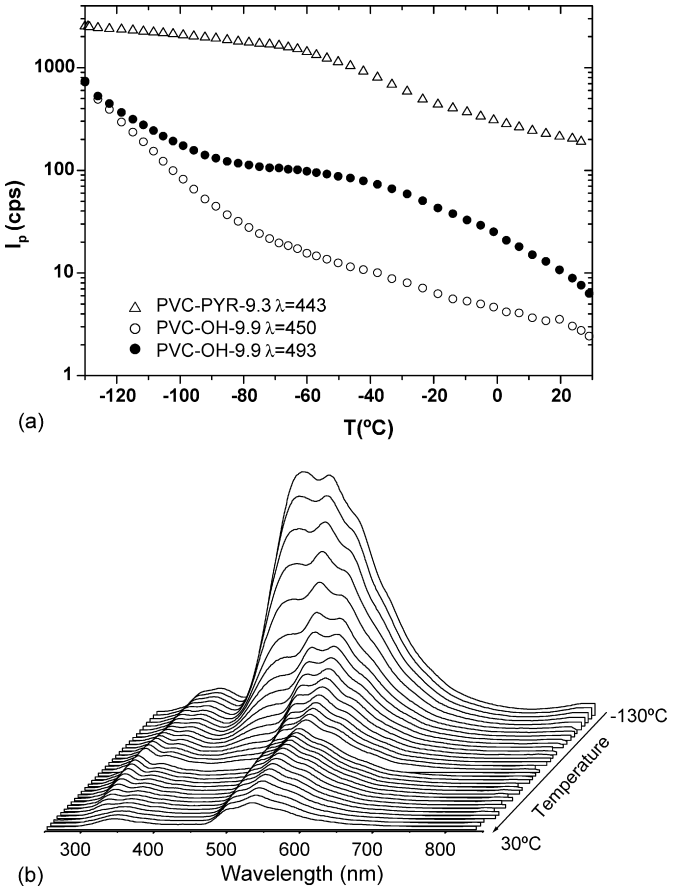


Fig. 7. (a) Phosphorescence decay of sample PVC-OH-9.9 as a function of temperature, as monitored at 450 nm and 493 nm compared to results for PVC-PYR-9.3; (b) spectral evolution.

Fig. 6 corresponds to the phosphorescence of a very slightly modified sample, only a 3% of the chlorine atoms have been substituted by 4-mercaptophenol. The PVC-OH-3 emission at low temperature (Fig. 6b) is constituted of several bands in the range 440 nm and 600 nm (440 nm, 482 nm, 525 nm and 575 nm). As temperature increases, the component at 450 nm quickly disappears, yielding a spectrum with peaks at 490 nm, 524 nm, 575 nm, not further modified by the increase of temperature over −80 °C.

Fig. 6a confirms the existence of two different decay kinetics: when monitoring the phosphorescence at 440 nm a very quick decay taking place from the lowest temperature is registered (−130 °C). At −40 °C the luminescence intensity has almost reached the noise level. However, if the phosphorescence is monitored at 484 nm, the decay behaviour is more complex, as a quick decay from −130 °C to roughly −80 °C occurs, after which a gentle decrease similar to that observed in PVC-PYR takes place. A β relaxation is detected between −60 °C and −30 °C.

Fig. 7 shows the phosphorescence decay and spectral evolution of PVC-OH-9.9. The spectra and overall behaviour of PVC-OH-9.9 is very similar to that of PVC-OH-3.0, except that in the former the first spectrum at −130 °C is slightly less intense at 450 nm relative to 490 nm than in the latter. This relative

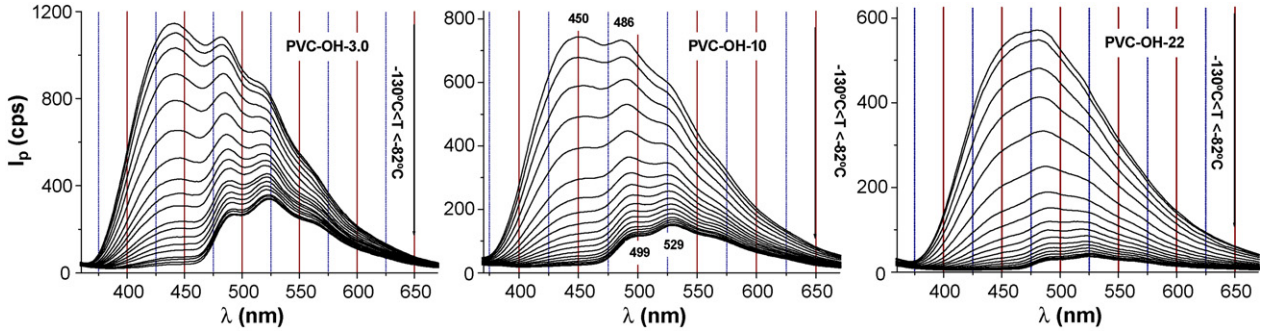


Fig. 8. Spectral evolution of samples PVC-OH-3.0, PVC-OH-9.9, and PVC-OH-21.7.

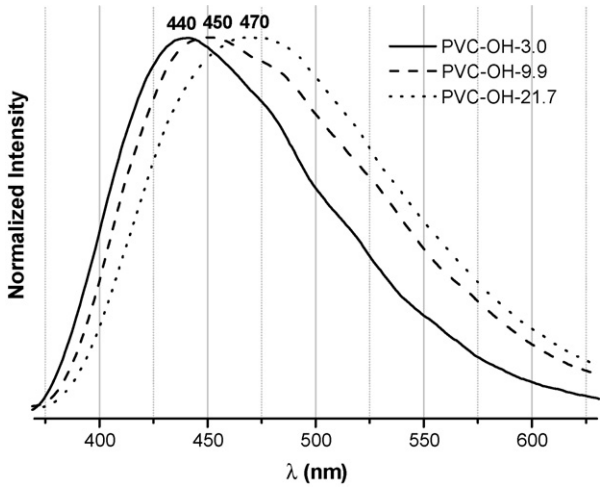


Fig. 9. Result of subtracting the spectrum recorded at −80 °C to the one obtained at −130 °C for the PVC-OH samples.

decrease of the 450 nm component is even more conspicuous in PVC-OH-21.7 (Fig. 8).

A summary of the spectral evolution of phosphorescence in the PV-OH series is shown in Fig. 8. As the probe concentration increases, the relative importance of both the emission at 440 nm and of the structure at 490–525–560 nm decreases and the maximum of the emission shifts from 440 nm to 475 nm. The 440 nm emission is very sensitive to temperature (through deactivation by rotation of the side group), and disappears between −130 °C and −80 °C. The structured emission is much less sensitive to temperature, behaving in this sense in a way similar to the PVC-PYR or PVC-NAPH.

In Fig. 9, the spectrum of the phosphorescence which is quickly decaying in the range −130 °C to −80 °C in the PVC-OH samples has been isolated. This has been done by subtraction of the spectrum recorded at −80 °C from that obtained at −130 °C for samples PVC-OH-3.0, PVC-OH-9.9 and PVC-OH-21.7. It should be noted that the component which disappears quickly between −130 °C and −80 °C progressively broadens and shifts to higher wavelength as the modification degree of the sample increases. The shift is by 30 nm when going from the less concentrated sample to the most.

The hypothesis has been made that in PVC-PYR and PVC-OMe the low wavelength component (at roughly 440 nm in both cases) corresponds to a phosphorescence emission from isolated entities. There is another emission in both samples at roughly 490 nm, which has been ascribed to aggregates in the fundamental state in the case of pyridine and to excimers in the case of 4-methoxybenzenethiol. As explained before, isolated entities in PVC-PYR are more sensitive to motions in the PVC environment than the aggregated species, as the former are surrounded solely by PVC while the latter are in a local environment made of PVC and pyridine modified PVC. This explains why along the β relaxation it is this component at 440–450 nm corresponding to isolated probe bearing entities which disappears more quickly. In the case of PVC-OMe, on the other hand, the ascription of the component at 450 nm to isolated entities and the fact that a non-radiative deactivation path exists in this probe via the onset of rotation of the methoxy side group, explains why most of the probe is deactivated at low temperatures and why the remaining spectrum above −80 °C shows peaks at 490 nm.

In the case of PVC-OH, the emissions can be divided into two groups: those which disappear over −80 °C and those that remain conspicuous up to ambient temperature. The first group has the characteristic of being short lived ($\tau < 40$ ms) as compared to the latter ($\tau > 0.3$ s). We will discuss them separately.

3.2.4.1. The 440 to 490 nm short lived emissions. These short lived emissions resemble strongly the ones found in the other two probes: at low probe concentration it peaks at 440 nm, and as the concentration increases a shift occurs to higher wavelength (Fig. 9). As the spectrum is broad, it is not easy to decide if the emission is related to only one process, as would be the case for example if the environment of the chromophores is progressively changing on increasing modification degree, or if there are actually two bands, peaking at roughly 440 nm and 480 nm, and whose relative contribution is changing on increasing modification degree. Given the shape of Fig. 9, with shoulders detectable at the two aforementioned wavelengths, and the behaviour of the other probes, the second hypothesis is privileged and results are discussed on this basis. Again, the lower wavelength emission can be attributed to isolated probes, while the latter can be ascribed to aggregates or excimers.

In support to this hypothesis, Fig. 10 shows the development of hydrogen bonding detected by IR spectrometry as the probe concentration increases. Two main absorptions, ν_{st}(OH), are seen at 3532 cm^{-1} and 3327 cm^{-1}. The latter corresponds to hydroxyl groups interacting with the medium (the medium being either the chlorinated environment or other probes) and the former to hydroxyl moieties isolated in an apolar environment. The calculation of the corresponding band areas shows that the concentration of isolated hydroxyl groups remains constant in absolute value while that of "interacting" hydroxyl groups increase progressively as the concentration of the probe does so (Fig. 11). Thus, as the concentration of the grafted phenol probe increases, the intermolecular interaction as indicated in the FTIR

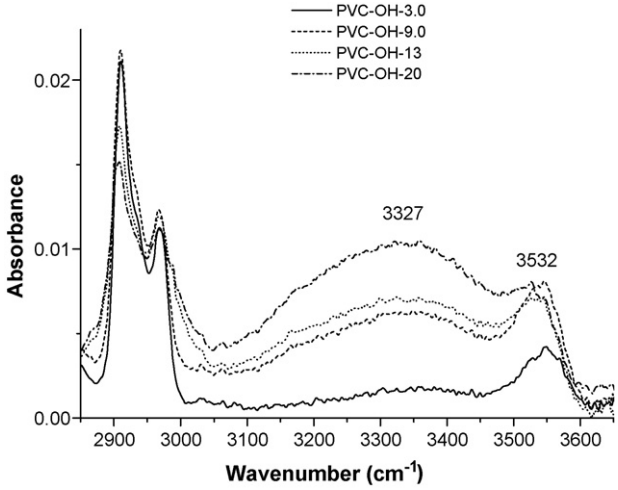


Fig. 10. ATR-FTIR spectra of the PVC-OH series.

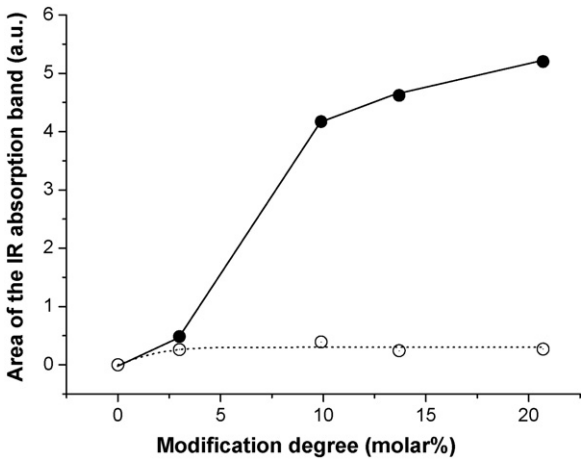


Fig. 11. Area of free and interacting hydroxyl groups as a function of the molar substitution degree: (●) band at 3327 cm^{-1} and (◯) band at 3532 cm^{-1}.

spectra by the ν_{st}(OH) band at 3327 cm^{-1} increases and the phosphorescence at −130 °C shifts from 440 nm to 473 nm. This supports the assignment of the 470 nm component of PVC-OH spectra to interacting/concentrated probes.

The luminescent properties of phenol and of phenol containing structures have been a matter of study for a long time. In particular, strong modifications of phosphorescence and fluorescence in hydrogen bonded and free phenols exist. The luminescent features of free phenol, phenol involved in water clusters and phenol in dimers have been thoroughly studied [17–19]. It has been shown that the probability of internal conversion, which in free phenol is abnormally high, is strongly decreased in the interacting phenol. This is because vibrational modes in which free hydroxyl groups are involved, are responsible for the high internal conversion probability of the singlet S_1, which mostly decays in this way. However, in interacting phenol, the decay of the singlet is due largely to intersystem crossing. A straightforward implication is that phosphorescence as compared to fluorescence is much more important in interacting phenols than in free phenols. No direct correlation can therefore be made as to the concentration of each species from the relative intensities of their phosphorescence emission.

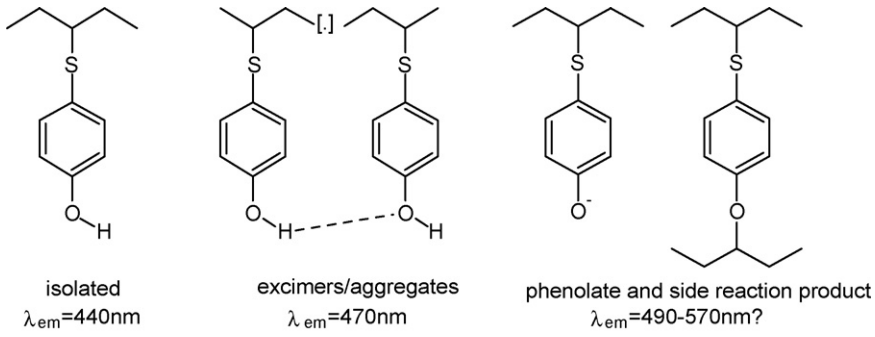
Emissions in the range 440–490 nm quickly disappear on increasing temperature from −130 °C, and at −80 °C they have completely vanished. Efficient non-radiative pathways must exist that allow the probe to relax at such low temperatures. In the case of the isolated phenol probe, this can occur via the rotation of the hydroxyl group; in the case of "concentrated" probes, it has to be taken into account that the phenol probe is forming hydrogen bonds with nearby phenol probes. It has been shown [20] that monohydroxy derivatives of benzophenones when strongly associated by hydrogen bonding deactivate readily due to fast non-radiative relaxation via hydrogen stretching vibrations in intermolecular hydrogen bonding. The same phenomenon can occur in strongly associated phenol probes grafted in PVC.

3.2.4.2. The 490 to 570 nm structured long lived emissions. The structured emission with longer lifetime is absent in PVC-PYR and in PVC-OMe. Surprisingly it is extremely similar (though slightly blue-shifted) to that of the naphthalene substituted PVC [7]. Even more, an emission with very similar features (long wavelength, structured and long lived) has been found by many authors in PET [21]. In fact, in the mentioned work it was discussed as one of the possible origins for this emission the presence of naphthalene groups, though it was discarded, as has to be now discarded. In our case, this structure is especially interesting, as it is this emission that allows to detect the β relaxation in mercaptophenol substituted PVC.

Multiple origins of this structured emission can be thought of: the existence of impurities of the nucleophile used in the substitution of chlorine atoms in PVC, the presence of solvent traces strongly bound to the grafted probes or the existence of side reactions leading to the formation of by-products are some examples. The phosphorescence spectra of the nucleophile in solution in ethanol and dichloromethane and of the solvents used in the reaction have been recorded and no such structure has been found. It has to be borne in mind that as the concentration of probe grafted to the PVC chain increases, both the low wavelength emission ascribed to isolated phenol probes and the highly structured emission decrease, while the emission at 470 nm due to interacting probes increases (Fig. 8) relatively and possibly also absolutely. Thus, the species responsible for the structured emission seems to be somehow correlated to the presence of isolated phenol. As mentioned in the preceding section the excimers or aggregates formed as the probe concentration increases may be quenching the emission from the chromophores which are more conspicuous at low probe concentration, i.e., no direct connection can be made between emission relative intensity and the relative chromophore concentration in the PVC chain. Still, there seems to be a correlation between the intensity of the lowest wavelength emission and that of the highly structured one.

The hypothesis of the existence of a by-product produced at the first stages of the reaction was checked. The reaction medium contains the solvent (cyclohexanone), the nucleophile, K_2CO_3, and PVC. The first probes grafted to the chain have a very high probability of being isolated (not involved in a hydrogen bond with other grafted probes); the acidic nature of phenol and the reaction medium make it possible for a fraction of the isolated phenol probe to be in the phenolate form. As the involvement of the phenol in a hydrogen bond reduces strongly the probability of hydrogen abstraction, the relative concentration of phenolate (always very small) will be higher the lower the probability of phenol probes interacting with one another via hydrogen bonding. In short, the relative concentration of phenolate will be higher the lower the absolute concentration of grafted probe. Thus, when the concentration of grafted probe is very small, the dominant species will be isolated phenols and a fraction of isolated phenolates; as the probe concentration increases, so will the excimers/aggregate concentration do, at the expense of isolated mercaptophenols or mercaptophenolates.

Although it has been shown that mercaptophenol under the chosen modification reaction conditions is extremely selective with respect to the mercapto group, small amounts of phenol groups may also substitute chlorine in the PVC chain in such a way that the probe will be grafted onto the polymer chain at two points, by a mercapto and an ether bridge. This by-product has no



Scheme 2.

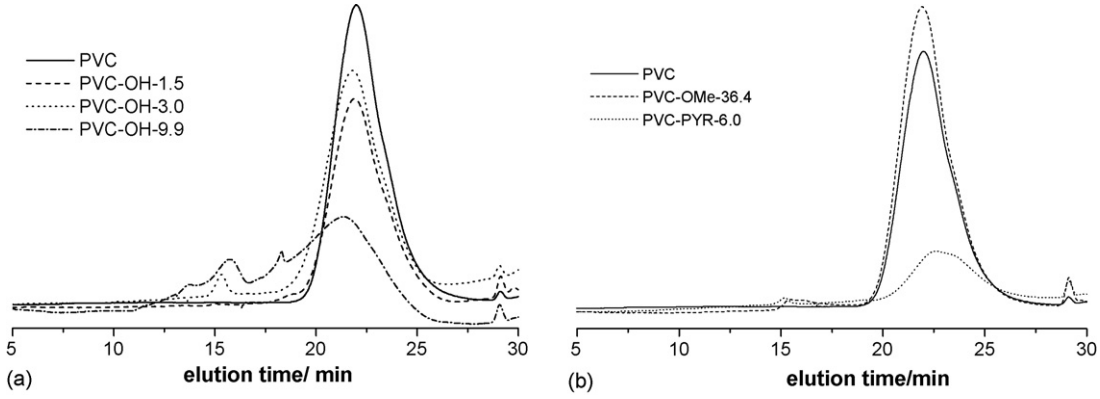


Fig. 12. SEC traces of PVC and some PVC copolymers: (a) PVC-OH series and (b) PVC-OMe-36.4 and PVC-PYR-6.

side group able to rotate and is incapable of forming a hydrogen bond. Deactivation of this chromophore via non-radiative paths is very limited. This hypothesis would explain why the structured emission is only mildly sensitive to temperature and able to detect the β relaxation. The emitting species proposed in PVC-OH appear in Scheme 2.

An obvious consequence of the preceding hypothesis is the rise in molecular weight of a part of the original PVC sample. SEC analysis was done in order to check if substantial modifications of the molecular weight occur as the PVC chain is modified. Fig. 12 shows the results obtained.

Fig. 12a shows a progression of SEC traces corresponding to the PVC-OH family. The development of two shoulders at lower elution times indicates the existence of higher molecular weight fractions. This does not occur in the PVC-PYR or PVC-OMe series, as shown in Fig. 12b. We conclude, then, that the structured emission in the phosphorescence spectra of PVC-OH is related to a side reaction which leads to the grafting of the probe both by the mercapto bridge and the ether bridge. These units are, by their own nature, isolated and closely connected to the motions of the PVC chain, what explains the sensibility of the emission to the low temperature dynamics of PVC.

4. Conclusions

In this and a preceding work, the spectral evolution and intensity variation as a function of temperature of the phosphorescence of probes grafted onto PVC in increasing concentrations have been studied. Two aspects have to be carefully considered when investigating the local structure of a glass by means of a luminescent probe. The first aspect is that the grafting of the probe alters the microenvironment of the polymer precisely at the site where the probe will be active. This was the scope of the preceding work. The second aspect which has to be carefully considered is the probe itself. Local sub-T_g relaxations in a larger number of polymers occur under room temperature down to −100 °C or less. Processes like hydrogen abstraction, the rotation of small side groups or the vibration of intermolecular interactions may thus interfere with low temperature relaxations of glasses, and the decay kinetics can in some cases be the superposition of relaxations taking place in the probe and in the polymer in the same temperature range.

The probe concentration has also proved to be a critical parameter. Even if no strong interactions occur between the probes, the behaviour of “isolated” or “interacting” probes may be very different. Probes near to one another may form aggregates or dimers in the ground state, or excimers in the excited state, each with very different features. Side reactions at low probe concentrations, which lead to unexpected grafted probe structure may also take place.

The investigated probes, PVC-PYR, PVC-OMe and PVC-OH, exhibit a phosphorescence spectrum that red-shifts as the concentration of the probe increases. In the first case, it is so because of the formation of aggregates, in the second and third very probably because of the formation of excimers. The presence of a side group (PVC-OMe and PVC-OH) leads to efficient deactivation of the probe (either isolated or interacting chromophores) at very low temperatures ($T < -80$ °C), making it

impossible for the β relaxation to be detected. The presence of a phenol group introduces a more complicated panorama, because of the acidity and reactivity of the side group. Side reactions are very probably responsible for the presence of a small amount of a by-product responsible for a structured phosphorescence emission in the range 490–570 nm, a process which is conspicuous up to ambient temperature and which is sensitive to the local motions taking place at the β relaxation of PVC.

This relaxation can then be followed by monitoring the whole emission of the naphthalenethiol and mercaptopyridine probe and the long wavelength emission of mercaptophenol.

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