Secondary Relaxations in PVC As Studied by Phosphorescence Decay of Grafted Luminescent Probes

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ABSTRACT: Secondary relaxations have been detected in poly(vinyl chloride) (PVC) by measuring the phosphorescence emitted by chromophores present as defects in the polymer chains and in PVC with luminescent probes, pyridine and naphthalene, grafted onto the chain. The measurement of phosphorescence decay with temperature allows to identify the existence of two components in the β-relaxation of PVC: one at about −40 °C and the other at about −60 °C. The progressive introduction of luminescent probes grafted on the PVC backbone and the study of such luminescent copolymers permits to attribute the well-known decrease of the β-relaxation intensity when grafting or plasticizing, to the progressive disappearance of the high-temperature component. The spectral analysis of the mercaptopyridine grafted PVC copolymer (PVC−PYR) in the temperature range −130 to −30 °C shows 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 sensible to the motions of contiguous unmodified PVC segments.

1. Introduction

This work presents a study on the determination of secondary relaxations by the measurement of the emission from grafted luminescent probes as compared to other more frequent methods, in particular dynamical mechanical analysis (DMA).

In polymers exhibiting both a glass transition and a secondary sub-T_g relaxation (β-relaxation) it has for long been observed that slight structural modifications (plasticization, external or internal) of the material which lead to a decrease in the temperature of the glass transition may also lead to an increase of the elastic modulus in the glassy state.[1,2] This phenomenon, called antiplasticization, has been observed in polymers such as polycarbonates,[3,4] aromatic backbone polymers,[5] epoxy resins,[6] PVC,[1,7] and others. A characterization of the sub-T_g relaxations reveals that, together with the decrease of the glass transition temperature, the progressive disappearance of secondary sub-T_g relaxations (β-relaxation) is also taking place. The consequence of the disappearance of the β-relaxation is an increase of the chain stiffness and of properties related to this structural feature, such as mechanical or dielectric response or molecular transport,[8] for example.

The decrease of the strength of the β-relaxation is very often related to the lowering of the temperature of the glass transition; even some hypothesis on the connection between both phenomena have been proposed,[9] especially as it seems that the high-temperature tail of the transition is mostly affected. The denomination of β-relaxations or secondary relaxations comprises extremely different phenomena, as the only requisite for relaxations being called β is that they precede the glass transition. In fact, in complex systems such as polymers, processes leading to relaxations in the glassy state are numerous and may be very different in nature. Excellent reviews and classifications can be found in the literature.[9,10] A very simple classification of β-relaxations in three groups can be made: secondary relaxations caused by motions involving side groups, secondary relaxations caused by motions involving a repeat unit or a small number of repeat units (local chain motions), and secondary relaxations caused by motions involving the entire molecule (Johari−Goldstein). Obviously, secondary relaxations in PVC must belong to the second and/or third group, as it contains no side groups. The characterization and classification of these secondary relaxations is necessary for accomplishing a better understanding of the glassy state, but not only; the temperature range at which many polymers are used is comprised between the T_β and T_α, and most properties are strongly affected by the presence, absence, or modifications of the secondary relaxation.

Luminescent sensors sensitive to changes of polarity, viscosity, and pH in their microenvironment have become a powerful tool to study different processes in polymers, such as polymerization kinetics,[11] swelling,[12] secondary relaxations and thermal transitions,[13] degradation processes,[14] etc. This is due to several advantages of the luminescence spectroscopy with respect to conventional techniques: high sensitivity and selectivity, very short time response ($<10^{-9}$ s), and its nondestructive character. Finally, processes that occur at different time scales may be studied in real time.[15] It has to be kept in mind that the features studied when measuring emission from luminescent sensors are those of the local environment of the probe and not of the overall material.

Secondary relaxations of polymers have been characterized using various methods, including mechanical and dielectric spectrometry, NMR, IR, and Raman spectroscopies. In the past decade the study of secondary relaxations by using luminescent probes for several

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polymers was reported in the literature.[16−18] It is based on the strong photophysical properties of the probe once incorporated in the polymeric material. If a luminescent probe is attached to a polymer segment involved in a relaxation, any change in the emission may be directly related to local changes in the matrix, as the macromolecular segment cooperative motions modify the photophysical processes of the fluorescent guest. Hence, the probe emission intensity depends on both its intrinsic photophysical properties and its interactions with the polymer matrix.

A decrease of the luminescent intensity with increasing temperature is generally observed. It was theorized that enhancement of the free volume of the medium leads to an increase in the nonradiative decay rate and consequently a decrease in emission quantum yield. Recently, probes have been used to study the α- and β-relaxation processes in poly(ethylene terephthalate) with different degrees of crystallinity.[14] The fluorescent probes have proved to be sensitive to the morphology of polymer samples, and their fluorescence properties strongly depend on the crystalline index.[14]

For the present investigation on the use of grafted luminescent probes as a means of studying local properties of polymeric materials, PVC has been chosen as the starting polymer as it is well-known that it can be modified chemically in a very controlled manner by nucleophilic substitution of its chlorine atoms when strong nucleophiles and appropriate reaction conditions are used.[19,20] It has, furthermore, been subject to a detailed analysis of the dependence of its microstructure, chemical composition distribution, and stereoregularity on modification with the nucleophiles used in this study. This is absolutely necessary as the grafted probe alters the local structure of the polymer, which constitutes one of the main differences with methods that do not require the introduction of a probe. For this reason, in fundamental studies on the relationship between polymer structure and properties, the gradual replacement of atoms or groups of atoms from the polymer chain by polymer modification reactions[21−23] and the gradual introduction of the probe accompanied by extensive characterization of the structural features constitute the most efficient and elegant procedure.

The structure/property analysis using luminescent probes, or rather, when taking advantage of the luminescent nature of the graft, is then complementary though not directly comparable to other techniques, such as mechanical or dielectric excitation. In the latter cases the effect of modification on β-relaxation is seen as far as it affects the mechanical response or as far as the ability of the C−Cl dipole to orient itself in an electric field is affected. In the case of the luminescence response, what is actually being monitored is the ability of the excited probe to deactivate itself via nonradiative paths. This procedure has obvious advantages: there is no need for dipoles to be present as in the case of dielectric spectroscopy, and there is no need either that the sample presents adequate mechanical properties as occurs in DMA. The incorporation of the luminescent probe or label grafted onto the polymer backbone has an additional advantage: when heating or cooling, no migration occurs. The incorporation of the probe by swelling modifies the matrix structure and may lead to ambiguous results.

In this work special attention will be paid to two characteristic features of this characterization method, namely, (i) the fact that the structure of the polymer is modified by the introduction of the luminescent probe and (ii) the local nature of the information provided by the emission.

Scheme 1

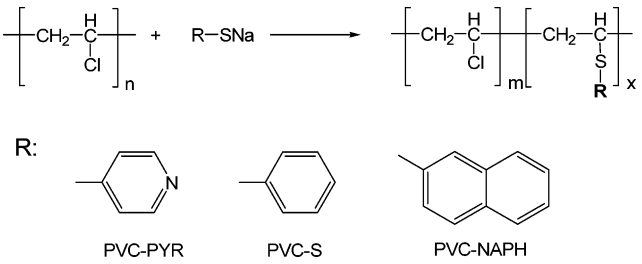

Table 1. Characterization of the Samples

name	modification	% grafting	thickness (μm) ± 3
PVC	none		50
PVC−PYR-9.7	pyridine group	9.7	42
PVC−PYR-26.2	pyridine group	26.3	60
PVC−PYR-31.4	pyridine group	31.4	53
PVC−PYR-43.1	pyridine group	43.1	55
PVC−NAPH-3	naphthalene group	3	37
PVC−NAPH-7	naphthalene group	7.2	20

2. Experimental Part

2.1. Materials. Commercial bulk polymerized PVC with a weight-average molecular weight of M_w = 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%.

Modification of PVC. 0.5 g (8 mmol) of PVC and 8 mmol of sodium salts of the corresponding mercapto compounds obtained by reaction with sodium hydride according to a procedure described elsewhere[24] were dissolved in 50 mL of cyclohexanone, and the reaction started under a N_2 atmosphere at 60 °C.

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 modified samples) as a solvent−precipitant system. The structure of modifiers and copolymers used in this work are depicted in Scheme 1. The grafting percentage is determined using H NMR spectroscopy. GPC measurements were used to determine the molecular weight of neat and modified PVC. The mercaptopyridine and mercaptonaphthalene series will be referenced to as PVC−PYR and PVC−NAPH hereafter. A detailed sample description is given in Table 1. Films were prepared by casting of THF solutions and subsequent drying.

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 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 realized using a homemade apparatus as described elsewhere.[25] The UV excitation was provided by 150 W xenon source coupled to a double-pass monochromator (Jobin-Yvon type H10). The available range of excitation wavelength was 220−800 nm with bandwidth of excitation of ≈2 nm. The spectral analysis of the emitted light was made using a grating monochromator (Jobin Yvon CP200) coupled to a cooled CCD camera. The analysis range was 220−840 nm, and the resolution was 4.5 nm. A photomultiplier (model R943-02 from Hamamatsu) working in photon counting mode was used for the purpose of phosphorescence lifetime estimation. Using a

thermally regulated sample holder, we achieved measurements in the temperature range −130 to +45 °C. All photoluminescence measurements were made in a 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 vs temperature plots.

2.3. Microstructure of Modified PVC. The chemical composition distributions of PVC modified with sodium thiophenolate (PVC−S), PVC−NAPH, and PVC−PYR copolymers have been studied by ^{1}H NMR and ^{13}C NMR spectroscopy on a 300 MHz XL Varian spectrometer in deuterated nitrobenzene under standard conditions at 90 °C.[26]

2.4. Physicochemical Characterization of the Copolymers. *Density and FFV.* The densities of the films were determined by the flotation method at 20 °C using water and an aqueous solution saturated with $ZnCl_2$. The experimental error is less than 0.002 g/cm^3.

The fractional free volume (FFV) was obtained as follows:

$$\mathrm{FFV} = \frac{V - 1.3V_w}{V} \quad (1)$$

where V is the polymer specific volume and V_w is the specific van der Waals volume.

Glass Transition. The glass transition temperature was determined by calorimetric measurements carried out in a Perkin-Elmer differential scanning calorimeter DSC-7. Samples of about 10 mg were heated to 150 °C under a nitrogen atmosphere at 20 °C/min and quenched with a cooling rate of 200 °C/min. The T_g values reported were taken from the second runs (heating rate 15 °C/min) and correspond to the midpoint of the DSC curves measured from the extension of the pre- and posttransition baseline. More details on the physicochemical characterization can be found in previous work on these copolymers.[8]

3. Results

3.1. Structure of the Phosphorescent Copolymers. It is evident that the knowledge of the final structure of PVC after the introduction of the phosphorescent probe is essential for a correct interpretation of the data. A blocky or a random substitution of chlorine atoms in the polymer chain will lead to luminescent copolymers of different structure. This first section is devoted to the presentation of the structural features of the copolymers under study.

In Figure 1a the content of ClClCl, ClSCl, and SClS triads for various chemical compositions of PVC substituted with sodium benzenethiolate is shown. For all three series a near-random substitution is obtained. This is a general behavior for this type of substitution. Configurational aspects of the modification of PVC via nucleophilic substitution reactions have also been studied in detail.[27−30] These studies implied a systematic analysis by ^{13}C NMR spectroscopy of polymers formed by the reaction with aromatic thiol compounds. According to this study, isotactic triads are the most reactive sites for chlorine substitution, followed by heterotactic and syndiotactic triads, being the latter ones almost unreactive. This is shown in Figure 1b where the relative amounts of smm, mr, and rr triads are represented as a function of the degree of modification.

Furthermore, the possible influence of polymer modification on the degree of polymerization of PVC has been studied.[31] According to GPC analysis performed on the modified polymers, for all aromatic thiol modifiers and for any composition, the chain length of the obtained PVC is the same as that of the original PVC. This means that the modification reaction is limited to chlorine substitution and that neither chain scission nor prolongation takes place.

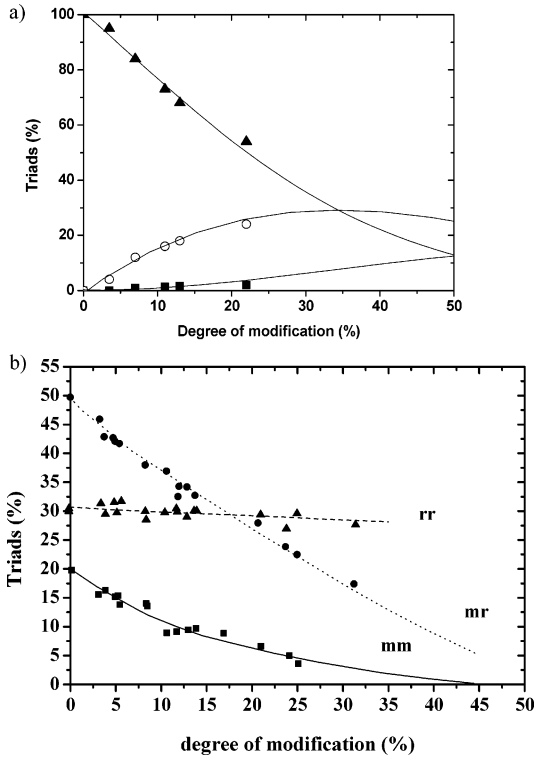

Figure 1. NMR data from PVC−S copolymers. (a) ClClCl (▲), ClClS (○), and SClS (■) triad fractions. Lines represent triad fractions in random copolymers (b) Dependence of the percentage of iso-, hetero-, and syndiotactic triads on the degree of modification of the polymer.

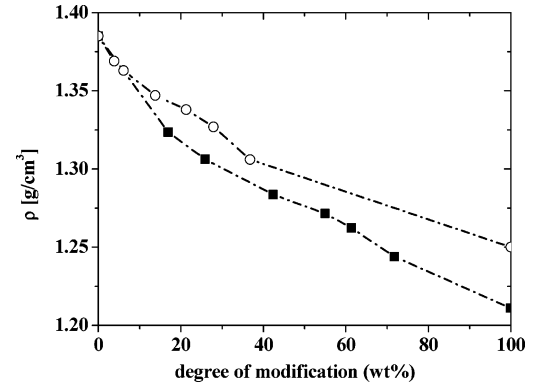

Figure 2. Density decrease as a function of conversion in wt % for samples PVC−NAPH (■) and PVC−PYR (○).

Density decrease is stronger the bulkier the size of the grafted probe[8] (Figure 2); however, this does not imply that the free volume in the system is higher, as this depends on the difference between the specific volume and the occupied volume. In fact, as shown in previous work for a set of copolymers, the fractional free volume (FFV) depends very little on the size of the grafted group.[8] This, though surprising, is indeed the case, and it has relevant consequences on other features directly related to phosphorescence decay, as for instance the free volume available in the immediate environment of the luminescent probe and the diffusivity of oxygen in these copolymers: both free volume and oxygen availability increase in the same way for naphthalene- and pyridine-modified samples. The glass transition temperature of these copolymers appears in Figure 3. The larger volume of the naphthalene group

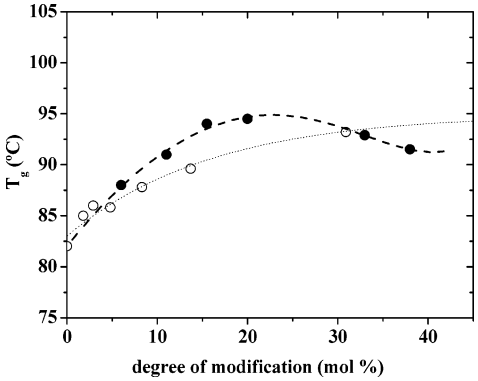

Figure 3. Variation of the glass transition temperature as a function of molar conversion for PVC−NAPH (●) and PVC−PYR (○).

is most certainly responsible for the stronger increase of T_g taking place in the PVC−NAPH copolymers.

In light of the data presented in this section, a final consideration on the structural features of the copolymers can be made. As regards microstructural evolution, random copolymers without blocky structures are obtained in the modification range under study (0−44%). Free volume and chain stiffness are increasing locally at the grafting site. The remaining PVC in the copolymers becomes more syndiotactic as modification increases, as the modification is stereoselective, being hetero- and isotactic triads preferentially modified.

3.2. Luminescence Features of Probes and Films. *Neat PVC.* Photoluminescence spectra of neat PVC consist of a weak emission in comparison to grafted materials, with fluorescence at 330 nm and phosphorescence at 425 nm. The excitation peak is at 280 nm for both. Neat PVC has no chromophores in its normal structure, and therefore the phosphorescence intensity is very low, the emitting species being defects of the structure. Homochain polymers (i.e., polyolefins, PVC, PS, etc.) possess C−C and C−H bonds that photooxidize, forming as the two most important species carbonyl and hydroperoxide groups. The carbonyl groups can be conjugated to double bonds, and these are the species responsible for the emission in this type of polymer.

PVC−NAPH. The absorption spectrum of the naphthalene-based probe shows vibrational structure, as expected in aromatic hydrocarbons such as naphthalene, and no shift of the maxima has been detected, either when changing the polarity of the solvent or when changing the concentration in the range 10^{-7}−10^{-4} M. The same occurs with phosphorescence at −196 °C. As a matter of fact, the spectra of the ungrafted and grafted probes are identical. Figure 4a shows continuous wave (CW) spectra obtained at 23 and −130 °C on a PVC−NAPH 7.2% film along with a decay spectrum recorded at −130 °C (the integration time with the CCD was 50 ms). Fluorescence is found at 359 nm and is no longer observed during the decay due to its short lifetime. Also, it can be noticed that at low temperature fluorescence represents only a weak contribution to the total signal. The structure of the phosphorescence contribution is clearly seen with bands at 497, 533, 568, and 625 nm. The corresponding lifetime has been estimated to 125 ms by PM measurements.

PVC−PYR. The pyridine-based probe displays a more complicated behavior. The absorption spectrum shifts to shorter wavelengths as the polarity of the medium increases (dichloromethane and ethanol), but it does no

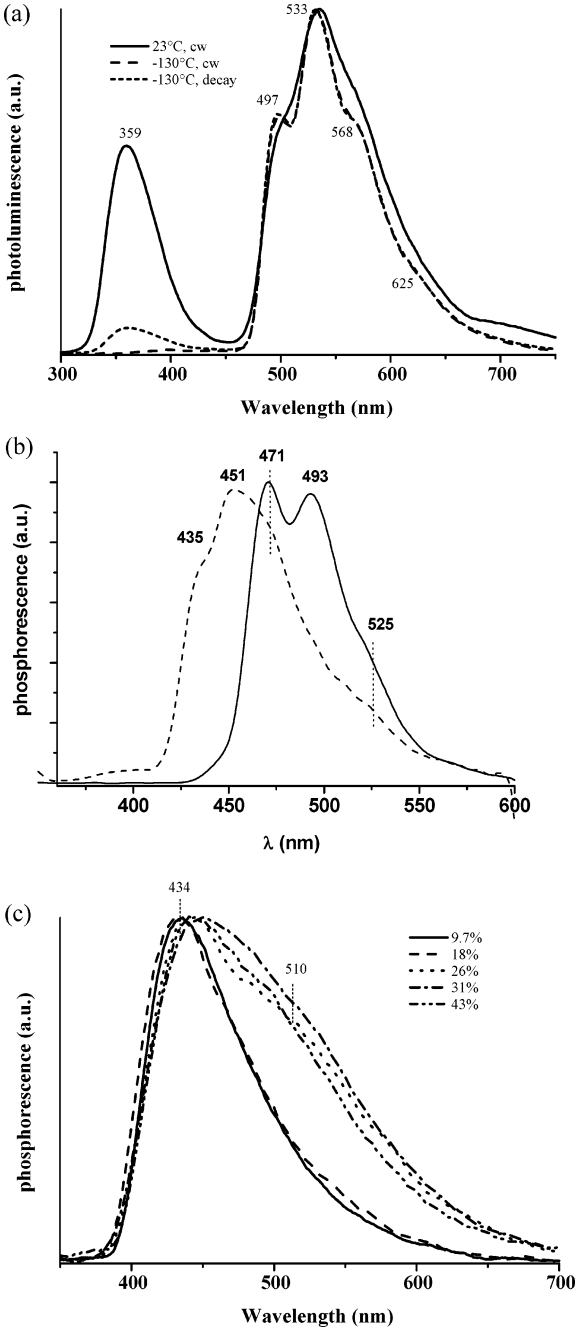

Figure 4. (a) CW photoluminescence spectra of PVC−NAPH-7.2 at different temperatures and phosphorescence decay spectrum, with excitation at 280 nm. (b) Phosphorescence in ethanol at 77 K of 1-mercaptopyridine at a concentration of 1.15×10^{-5} M (dashed) and 1.64×10^{-4} M (solid), with excitation at 340 nm. (c) Phosphorescence decay spectra of PVC grafted with 1-mercaptopyridine up to different molar conversions, with excitation wavelength of 320 nm and CCD integration time of 1 s.

vary with concentration. The phosphorescence at −196 °C in ethanol is quite strong, and the spectrum varies with concentration. Figure 4b shows the phosphorescence spectra of the pyridine based probe before grafting onto the polymer and as a function of the concentration in ethanol. At low (10^{-5} M) concentration four shoulders, at 435, 451, 471, and 525 nm, appear superposed on a broad envelope. As concentration increases, the shoulders at 435 and 451 nm disappear and are substituted by peaks at 471, 490, and 525 nm. In the literature, a red shift is attributed to the formation of aggregates as

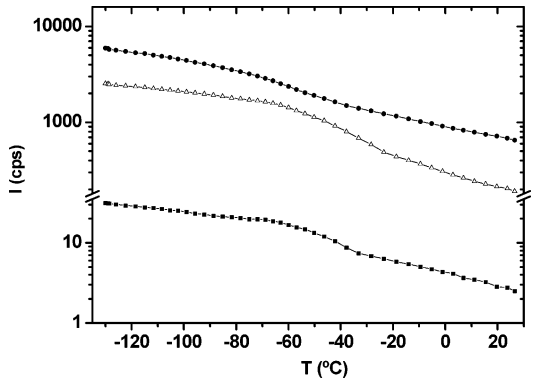

Figure 5. Phosphorescence intensity vs temperature for neat PVC (excitation at 250 nm) and PVC−PYR (excitation at 340 nm) samples recorded from −130 to 30 °C at a heating rate of 4 °C/min; cps stands for detector counts per second.

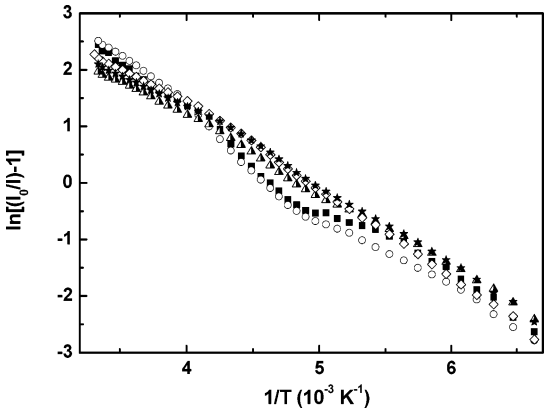

Figure 6. Phosphorescence decay in Arrhenius coordinates for PVC (■), PVC−PYR-9.7 (○), PVC−PYR-26.2 (△), PVC−PYR-31.4 (◇), and PVC−PYR-43.1 (★). Io is the intensity at low temperature.

concentration and mobility permit it.[32] For PVC−PYR copolymer films, two phosphorescence processes were identified: one in the range 425−440 nm, with excitation maximum at about 310−320 nm, and one emission at 500−510 nm (excitation at 270−280 nm). The corresponding lifetimes have been estimated roughly to 40 and 120 ms, respectively. An example of decay spectra for various modification degree is shown in Figure 4c. As the modification degree increases, the trend is a strengthening of the emission at about 500 nm. This trend appears consistent with results obtained in solution, the lower wavelength contribution being relevant to isolated species and the longer wavelength one reflecting interactions between nearby chromophores, as a result of aggregates or excimers formation.

3.3. Phosphorescence Decay as a Function of Temperature. In this section, the temperature evolution of the overall phosphorescence and its spectral features are shown for neat PVC, PVC−PYR, and PVC−NAPH.

Pyridine-Modified PVC Samples. Figure 5 displays the phosphorescence intensity of neat PVC as a function of temperature. The phosphorescence emission is smaller the higher the temperature, an expected behavior, and in the range −70 to −30 °C a double change in slope is seen. In the same figure, two experiments performed on PYR−PVC are shown: as expected, the PYR−PVC samples show a much stronger emission, and more so the greater the degree of modification. A double change in slope is also seen very clearly though at a different

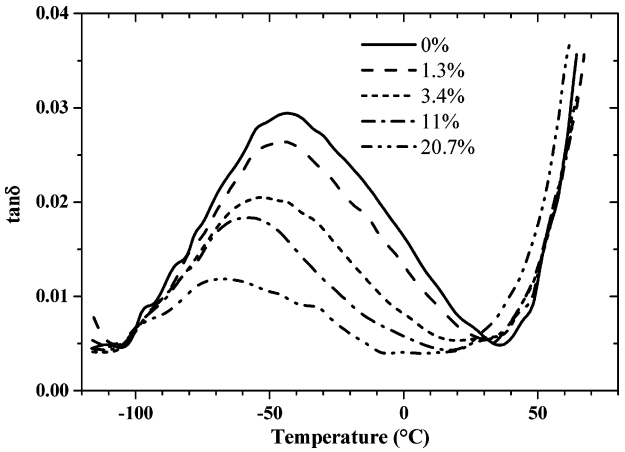

Figure 7. Mechanical loss factor (f = 3 Hz) showing the β-relaxation of PVC and modified PVC with various conversion degree of sodium thiophenolate (PVC−S).

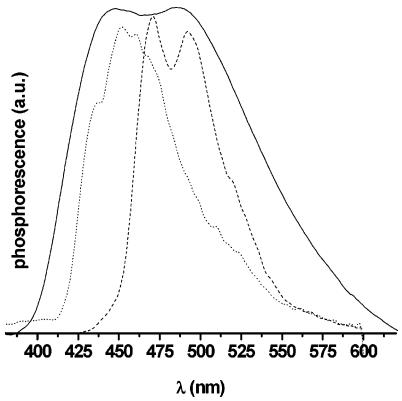

Figure 8. Phosphorescence spectrum of the ungrafted mercaptopyridine probe at low (dot) and high (dash) concentration in ethanol at 77 K compared to the phosphorescence spectrum of PVC−PYR-9.7 at −130 °C.

temperature interval; the midpoint of these two samples would be at −44 and −61 °C, respectively, i.e., at a lower temperature as the degree of modification increases. In addition, as modification increases, the change in slope gets smaller. Figure 6 shows the phospho decay of all the PVC−PYR samples represented in Arrhenius coordinates, using the representation of Somersall et al.[33] The same features are seen as in the linear comparison performed in Figure 5.

The double change in slope which is seen in neat PVC and in modified PVC is most probably the well-known β-relaxation of this polymer. As shown in Figure 7,[7,34] in mechanodynamical experiments at 3 Hz and a heating rate of 2 °C/min it appears in PVC at about −50 °C and in a broad temperature interval, from about −120 to 30 °C.[31] The midpoint of the relaxation as seen by phosphorescence decay is at about −46 °C. Figure 7 also shows that the effect of progressive substitution of chlorine atoms by a nucleophile (in this case sodium thiophenolate) is a decrease of the relaxation intensity which occurs mostly from the high-temperature side, what brings about a shift of the maximum to lower temperatures. This is in agreement with the data shown in Figures 5 and 6, which show how the slope change gets smaller and shifted to lower temperatures as the modification degree increases. In the work cited before,[7] it was proposed that the motions giving rise to the β-relaxation could take place at the end of isotactic sequences (mmr). Taking into account their relative

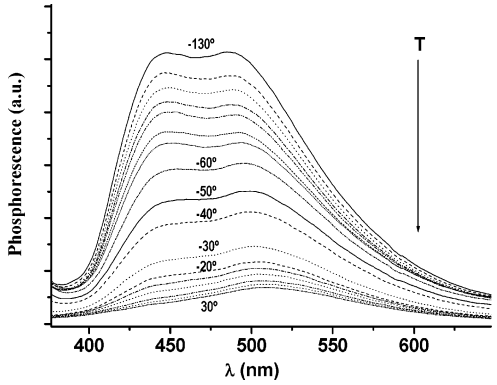

Figure 9. Phosphorescence spectra of sample PVC−PYR-9.7 as a function of temperature.

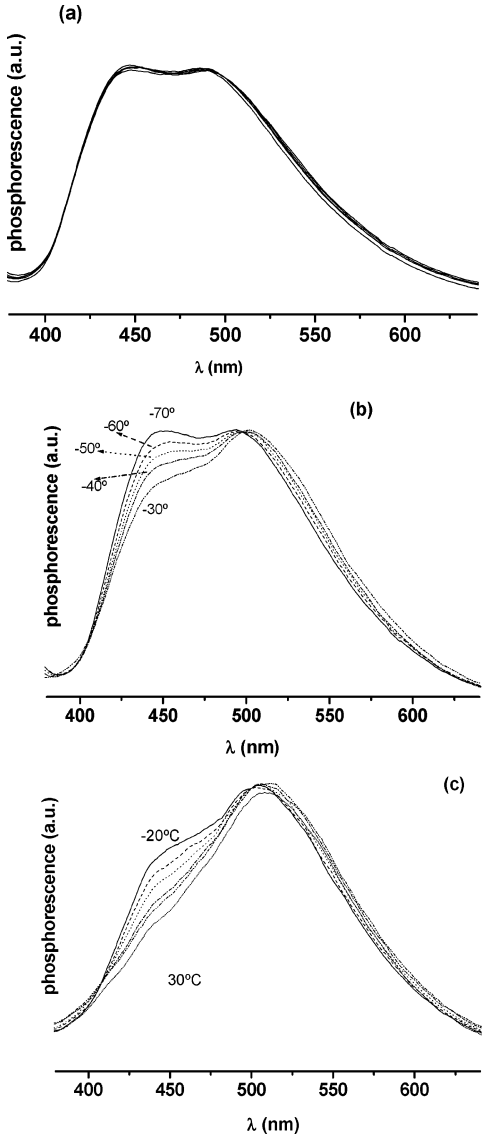

Figure 10. Phosphorescence spectra of sample PVC−PYR-9.7 at 10 °C temperature intervals: (a) from −130 to −90 °C; (b) from −70 to −30 °C; (c) from −20 to 30 °C.

abundance (see Figure 1b) in the PVC chain (50%), the evolution of the mechanical β-relaxation as modification proceeds (Figure 7) and their progressive decrease as modification increases (Figure 1b), this seems very likely.

Figure 8 shows the spectrum of the light emitted at −130 °C by the mercaptopyridine grafted sample PVC−

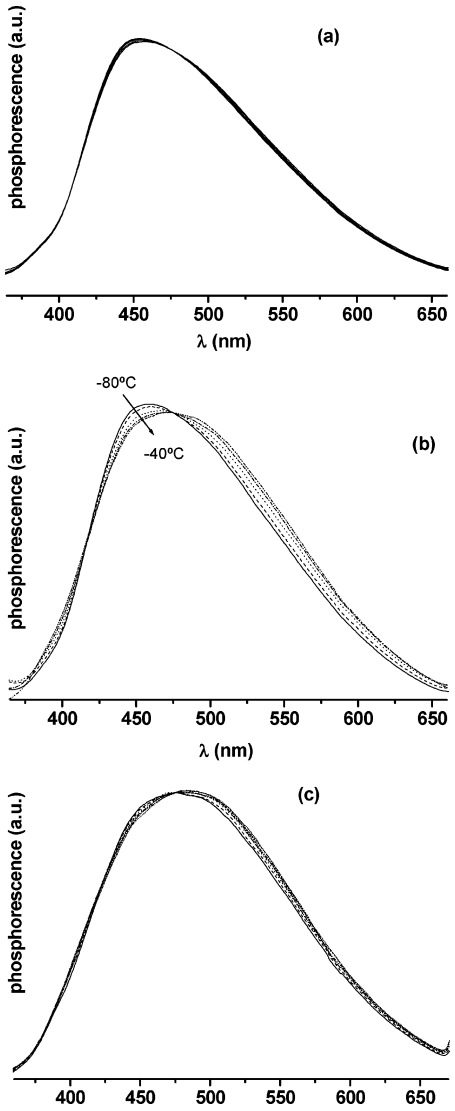

Figure 11. Normalized phosphorescence spectra of sample PVC−PYR-43.1 at 10 °C temperature intervals: (a) from −130 to −90 °C; (b) from −80 to −40 °C; (c) from −30 to 30 °C.

PYR-9.7 as compared to the emission by the ungrafted probe in ethanol at −197 °C. Both the emissions from isolated species and aggregates or excimers appear in the spectrum of the grafted probe, though they do not appear resolved. Figures 9 and 10 show the spectral evolution of phosphorescence as a function of temperature as obtained and normalized, respectively. Between −130 and −80 °C (Figure 9), though the overall intensity is progressively decreasing, there is no significant change in the relative intensity of both envelopes. Between −70 and 0 °C, however, it is the component at lower wavelength which suffers the strongest decrease, and from 1 °C onward no significant changes in the spectrum are seen. Attending to the assignation of bands performed before, it is the isolated entities which are being affect by the β-relaxation, either because segments of PVC incorporating isolated entities are still able to relax or because the microenvironment of the probe is relaxing. On the other hand, probes which are interacting with each other are no longer reflecting the β-motion because the β-motion is not possible in those segments or because their microenvironment is not relaxing either.

For the other three degrees of modification (PVC−PYR-26.2, PVC−PYR-31.4, PVC−PYR-43.1) the same

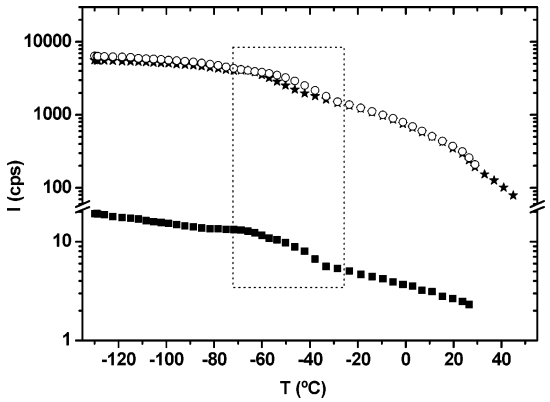

Figure 12. Phosphorescence intensity vs temperature for PVC (■), PVC−NAPH-3 (○), and PVC−NAPH-7 (★) heated from −130 to 50 °C at a heating rate of 4 °C/min.

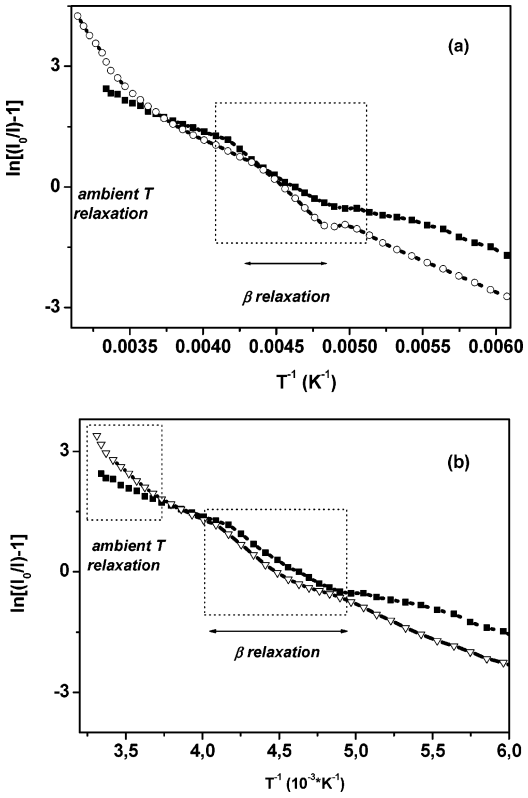

Figure 13. Phosphorescence decay in Arrhenius coordinates for PVC−NAPH-3 (○) and PVC−NAPH-7 (▽) compared to that of neat PVC (■).

experiments have been performed, and the same effect is seen. As an example, Figure 11 shows the normalized spectra of PVC−PYR-43.1. In this case the low wavelength decrease is less conspicuous. This is reasonable if the amount of isolated entities is very low, what most certainly must happen when almost half of the PVC repeating units has been substituted by the graft. Again, for temperatures above −30 °C, the spectra do not suffer important shape modifications.

Naphthalene-Modified PVC Samples. Figure 12 shows the semilogarithmic representation of the phospho decay in naphthalene-modified PVC samples as compared to neat PVC. Again, the modified samples show a much stronger emission than PVC, and the higher the modification (PVC−NAPH-7) the higher the luminescence intensity. The temperature range in which the relaxation appears is slightly shifted to higher temperatures as compared to that of PVC.

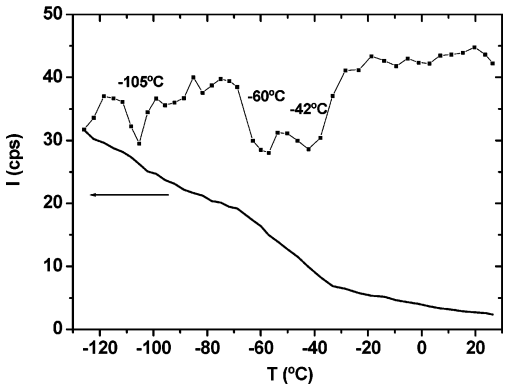

Figure 14. Phosphorescence decay and its first derivative for PVC.

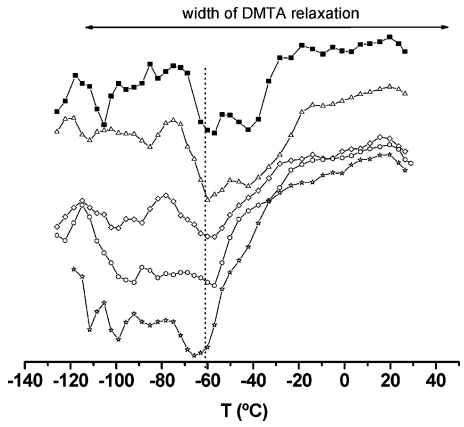

Figure 15. First derivative of the phosphorescence decay for PVC (■), PVC−PYR-9.7 (△), PVC−PYR-26.3 (◇), PVC−PYR-31.4 (○), and PVC−PYR-43.1 (★).

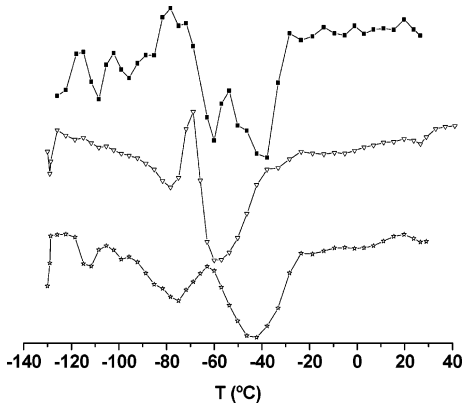

Figure 16. First derivative of the phosphorescence decay of PVC (■), PVC−NAPH-3 (▽), and PVC−NAPH-7 (★).

The spectra of phosphorescence do not change in shape at the β-relaxation; as temperature increases, the only modification seen in the spectrum is a gentle loss of the highly resolved vibrational structure.

For a better illustration of the evolution of the β-relaxation as modification proceeds, the first derivative of the luminescence decay is shown in the next figures. As in these representations the scatter of the data is considerable, only qualitative rough features can be taken into consideration. Figure 14 shows the first derivative of the photoluminescence decay of PVC. The inflection points of the decay curves appear as minima in the first derivative. The first derivative of the PVC phospho decay is composed of two very clear minima, related to two inflection points, at −60 and −40 °C.

To a first approximation, and as shown in Figure 15, it can be assessed that the progressive introduction of the pyridine probe in substitution of chlorine atoms leads to the disappearance of the high-temperature conspicuous inflection point (−40 °C). The strong change in slope at −60 °C is less affected. Of course, if studying the relaxation by other techniques,[35] what does seem to happen is the disappearance of the high-temperature side of a unique relaxation and a shift to lower temperatures of the maximum of the relaxation.

4. Discussion

When considering the photoluminescence decay in neat or substituted PVC and its relationship to possible relaxations of the matrix, it has to be borne in mind that the emission being studied is originated at luminescent defects of the enone−ene type existing in normal PVC in the first case and at the luminescent probe introduced via a nucleophilic substitution in the second case. Whether the distribution of phosphorescent defects in the PVC chain is random or not is unknown; whether the microenvironment of the defects is, as regards secondary relaxations, similar to the overall matrix is also unknown. In the case of substituted PVC, an analogous situation occurs; for being the substitution reaction stereoselective and the microstructure of the modified chain segment quite different from that of normal PVC, it is not evident that the microenvironment of the modified triads can be considered as a correct representation of the overall polymer or not. Thus, whether a direct comparison between this kind of "local" measurement (phosphorescent emission from emitting probes) and other macroscopic techniques, such as DETA, DMTA, or DSC, can be made is questionable. The coincidence between the results obtained in this case by both techniques is, in light of what has been exposed above, both surprising and noteworthy. It is very probably caused by the fact that the molecular origin of the β-relaxation and the site at which the phosphorescent probe is introduced coincide to a high extent; it was proposed[7] the end of a isotactic sequence, which comprises a hetero- and an isotactic triad, is involved in the motions giving rise to the β-relaxation, and the chlorine atoms which are substituted initially and up to high modification degrees are located at the same site. Therefore, the microenvironment shown by these probes is in this case a correct representation of the behavior of the polymer as regards this property. In this sense, the results of the pyridine-modified PVC spectra are very useful, as they show that only probes isolated in the chain reflect the existence of a β-relaxation. Probes forming part of blocky structures are not able to show the β-relaxation, very likely because only PVC segments relax at that temperature.

By studying the β-relaxation by means of a luminescent probe such as the naphthalene-based one, it cannot be assessed whether modified segments of PVC relax or not, as this probe gives no separate information on isolated and interacting chromophores. However, the spectra of the PVC−PYR series show that "diluted" or isolated chromophores are sensitive to the β-motions to a much higher extent than "concentrated" or "interacting" units; motions taking place out of the range of the local environment of the probes will not be detected by this method.

The difference in behavior between the pyridine and naphthyl probes puts in evidence the considerations made along the previous section about the local nature of the relaxation studied by luminescence decay. Though most probably the strong change in slope in the range −80 to −30 °C taking place in all the cases (neat PVC, pyridine copolymer of different compositions, and naphthyl copolymer of different compositions) is related to the β-relaxation of the matrix, the intensity of the relaxation, the number of components, and the actual temperature position of each of them are clearly dependent on some or all of the following points: (i) stereochemistry of the grafting reaction, (ii) local structure modifications introduced by the graft itself (local free volume and stiffness), (iii) extent of the reaction (percent of probes introduced in the system), and (iv) nature of the probe itself.

5. Conclusions

The measurement of phosphorescence decay with temperature allows identifying the existence of two components in the β-relaxation of PVC: one at about −40 °C and the other at about −60 °C. The progressive introduction of luminescent probes grafted on the PVC backbone and the study of such luminescent copolymers permits to attribute the well-known decrease of the β-relaxation intensity upon grafting or plasticizing (antiplasticization) to the progressive disappearance of the high-temperature component of the relaxation. The spectral analysis of PVC−PYR copolymers in the temperature range −130 to 30 °C shows that "interacting" modified segments do not relax, while isolated probes do relax, either because isolated modified segments display the motions characteristic of the relaxation or because they are sensible to the motions of contiguous unmodified PVC segments.

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