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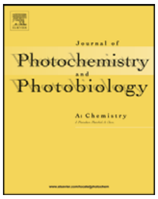

A chemiluminescence and fluorescence spectroscopy study: An investigation of photocrosslinking processes in polymer systems

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ABSTRACT

Chemiluminescence emission is shown to be a valuable method for the analysis and monitoring of the photochemical transformation process in BZMA-*co*-S copolymers. BZMA-*co*-S copolymer films are synthesized and irradiated at λ > 400 nm, in order to induce the phototransformation of benzyl (BZ) to benzoyl peroxide (BP) pendant groups, resulting in thermal decomposition and crosslinking. The chemiluminescence emission increases with irradiation time, and is shown to be related to the benzoyl peroxide moieties generated during irradiation. The increase in chemiluminescence intensity is interrupted at longer periods of irradiation, when the concentration of these species tends to a nearly constant value. In this case, others factors are considered to influence the chemiluminescence emission, for example the increasing crosslinking on irradiated samples, which would restrict the mobility of radicals to recombine due to crosslinking of the network.

A good correlation between fluorescence, FTIR and CL measurements during photochemical formation and thermal decomposition of peroxides is found. In this work, an intramolecular excimer forming fluorescent probe, DiPyM, is also used to analyse the crosslinking process. The results obtained contribute significantly to the development of chemiluminescence as a highly sensitive methodology for assessing the photocrosslinking of a polymeric material in the early stages of the process and is due to its sensitivity in comparison to that of fluorescence analysis.

1. Introduction

Benzil (BZ) derivatives are well-known Type II photoinitiators with benzil/amine systems having been used as photoinitiators for vinyl free radical polymerisation for many years. Some 1,2-dicarbonyl functionalised compounds are also industrially important as photoactive compounds for use in photoresists and photographic materials [1–3]. It has been shown previously, that the photochemistry of BZ was dependent on both, the employed irradiation wavelength and the absence or presence of molecular oxygen. The hydrogen atom abstraction by the lowest excited triplet state of benzil takes place in the absence of oxygen, leading to the formation of ketyl radicals from BZ and radicals from the hydrogen donor. However, it was recently reported that in the presence of oxygen, BZ could be converted almost quantitatively to benzoyl peroxide (BP) upon irradiation at λ > 400 nm, in solid polymer matrices such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). The later thermal decomposition of BP groups will then lead to the crosslinking of the polymer, Scheme 1. In fact, the vast majority of BP-based polymer chains were cross-linked even after irradiation without heating. This observation allows the application of polymers bearing covalently attached BP pendant groups for the preparation of photosensitive materials [4].

The aim of this work is to study the photochemical transformation of benzil carbonyl pendant groups in polystyrene copolymers, BZMA-*co*-S, to benzoyl peroxides carbonyl moieties, by using chemiluminescence and fluorescence spectroscopy. Recently, chemiluminescence (CL) has become a useful technique for the study of polymer degradation [5], oxidation mechanisms [6] and kinetics [7,8], as well as stabilizer efficiency [9,10]. This fact is due to its advantages with respect to other well-established techniques [11] especially its sensitivity. It is well known [12,13], that the chemiluminescence from polymers is due to the light emission that accompanies the recombination of secondary alkyl peroxy radicals. This bimolecular reaction promotes ketone products to its lowest triplet state and the radiative deactivation gives chemiluminescence emission in the visible region. The generation of peroxy radicals depends on the peroxide concentration, and the chemiluminescence emission can be related to the hydroperoxide (POOH)

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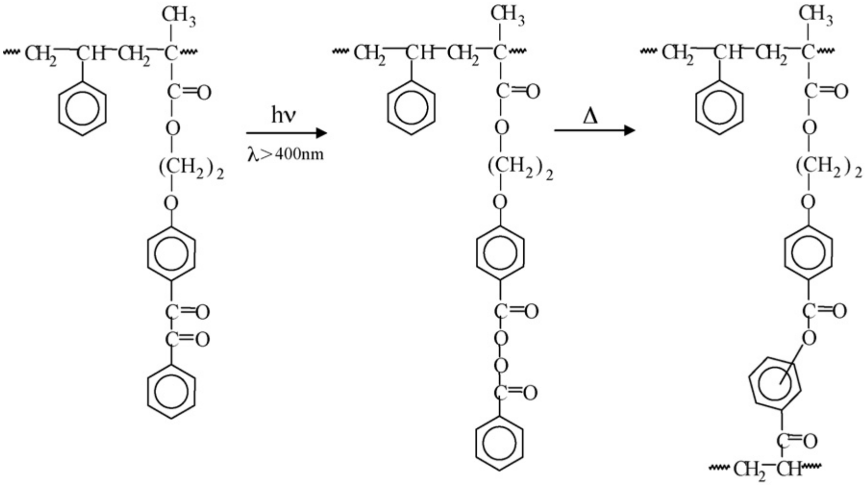

Scheme 1.

content, which are formed during processing or in-service life of the material under ambient conditions [6,14]. In previous work [15] the chemiluminescence emission has been shown to be sensitive to the morphology of polymer samples, which exhibit a strong dependence on the crystallinity. Therefore, chemiluminescence has been used to study relaxation processes in semicrystalline polymers. The chemiluminescence emission for example, decreases for poly(ethylene terephthalate) annealed samples with respect to the initial sample. In this work it was related to the enhanced crystallinity of annealed samples, which would restrict the mobility of hydroperoxides to react due to the higher rigidity of the medium.

The study of the chemiluminescence arising in the thermal decomposition of benzoyl peroxide in various polymers has been undertaken by a number of authors [16–18]. The recombination of benzoyloxy radicals or induced decomposition of benzoyl peroxide by benzoyloxy radicals has been proposed as chemiluminescence source, and the influence of factors such us composition, molecular weight and structure of polymers has been determined.

In the last decade, fluorescence analysis has also become a powerful technique for studying the properties of homopolymers, copolymers and blends by means of luminescent probes, which were incorporated, free or covalently attached, to the polymer matrix [19–22]. The emission of the fluorescent guest is sensitive to their microenvironment since the emission of the molecular luminescent probe depends on both their intrinsic photophysical properties and their interactions with the surrounding polymer matrix [5,6]. Thus, monitoring the UV curing of polymers [23], early stages of their photooxidation [11] as well as the swelling [24,25] gelation [25], crosslinking [26] and structure of interpenetrating polymer networks [24] are all processes in which the fluorescence technique has been successfully employed during the past few years.

For this purpose, an intramolecular excimer forming fluorescent probe, DiPyM, has been used to analyse the crosslinking process of BZMA-*co*-S films irradiated at $\lambda > 400$ nm, in order to follow the phototransformation of benzyl to benzoyl peroxide pendant groups, and their thermal decomposition and subsequent crosslinking. The fluorescence technique was also employed for monitoring excimer formation of DiPyM in cyclohexane, which was released from BZMA-*co*-S films on swelling. A range of cross-link densities was achieved through thermally treatment at different times of BZMA-*co*-S irradiated samples. In this way, copolymer films of different cross-link density may be characterised.

FTIR spectroscopy was used to measure the benzoyl peroxide moieties generated during irradiation and their decomposition upon thermal treatment and used to correlate the crosslinking results with those obtained by chemiluminescence and fluorescence analysis.

2. Experimental

2.1. Materials and sample preparation

The copolymer of 1-(4-(2-methacroyloxyethoxyphenyl))-2-phenyl-1,2-ethanedione (BZMA) and styrene (S), BZMA-*co*-S (M_n = 109,000 g/mol and M_w = 215,000 g/mol), was prepared as previously described in Ref. [27]. Films of BZMA-*co*-S were prepared via casting from chloroform solutions as described earlier [4].

The fluorescent probe di(1-pyrenylmethyl)ether (DiPyM) was synthesized as previously described in Ref. [28]. The structure of the probe used in this work is shown in Fig. 1. BZMA-*co*-S films doped with DiPyM were prepared by casting from chloroform solutions of the fluorescence probe (10^{-3} M).

BZMA-*co*-S films were irradiated ($\lambda > 400$ nm) using medium pressure mercury (or xenon) arc or in merry-go-round apparatus as described [2]. Thermal decomposition of the formed benzoyl peroxide structures was carried out in an oven chamber with air circulation at 91 ± 0.1 °C.

2.1.1. Chemiluminescence

Chemiluminescence spectra of film samples were obtained using an earlier described CL400 ChemiLUME apparatus from Atlas Electric Devices Co [29]. The film samples (4 mm diameter) were held in aluminium pans in the sample cell under a continuous flow of dry nitrogen (50 ml/min). The cell is temperature-controlled and was heated up with a pre-test ramp (10 °C/min) at 100 °C. During dynamic experiments, material samples are heated up to 200 °C with a heating rate (5 °C/min).

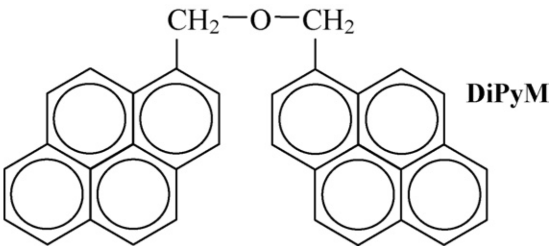

Fig. 1. Structure of di(1-pyrenylmethyl)ether (DiPyM).

2.2. Spectroscopic measurements

UV spectra were recorded by means of a PerkinElmer LS-35 spectrophotometer.

Fluorescence spectra were recorded by using a PerkinElmer LS50-B luminescence spectrophotometer.

Swelling by cyclohexane of polymer films with different crosslinking degrees was monitored by real time fluorescence spectroscopy. The emission analysis of extracted DiPyM was performed by placing the film at the bottom of the quartz cell of the spectrofluorimeter at 30 °C, and monitoring the formation of excimer by changes in its fluorescence intensity at 495 nm during swelling in cyclohexane.

FTIR spectra were recorded on NICOLET 400 FTIR spectrophotometer provided with a Fourier transform algorithm.

3. Results and discussion

3.1. Fluorescence behaviour of DiPyM adsorbed in BZMA-co-S films

Firstly, irradiation at λ > 400 nm of the copolymer film in the absence of a probe was undertaken, and the process monitored by means of FTIR and fluorescence. The phototransformation of benzil groups to benzoyl peroxide moieties can be easily followed by FTIR spectroscopy through the depletion of the absorption of the characteristic vibration of benzil groups and the subsequent formation of benzoyl peroxide groups. The FTIR spectra of BZMA-*co*-S irradiated at different times are presented in Fig. 2a.

The first feature from this data is the observation that the band corresponding to the 1,2-dicarbonyl groups at 1650–1700 cm^{-1} decreases progressively with irradiation time. In addition, a new absorption band appears in the 1750–1800 cm^{-1} region, which is associated with photogenerated benzoyl peroxide moieties [3]. The disappearance of 1,2-dicarbonyl groups can be expressed by Eq. (1):

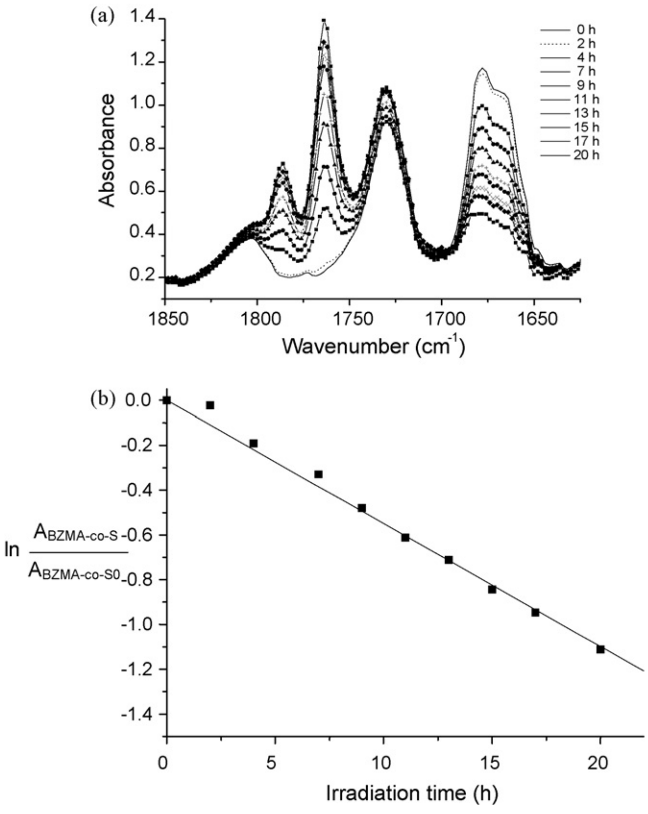

Fig. 2. (a) Changes in FTIR spectra of BZMA-*co*-S film upon irradiation at λ > 400 nm at different times and (b) the rate of benzil group depletion at 1678 cm^{-1}.

$$A_{\text{BZMA-}co\text{-S}} = A_{\text{BZMA-}co\text{-S0}}\, e^{-kt} \qquad (1)$$

where $A_{\text{BZMA-}co\text{-S0}}$ is the initial absorbance at 1678 cm^{-1}, $A_{\text{BZMA-}co\text{-S}}$ is the absorbance at time t, and k is the rate constant of transformation of the benzil bound to the polymer (BZMA-*co*-S) and to a benzoyl peroxide pendant polymer (BPMA-*co*-S).

Fig. 2b presents a plot of the decrease of BZMA-*co*-S copolymer versus irradiation time. A 70% decrease in the initial intensity was determined after 20 h of irradiation, and the rate constant of transformation of BZMA-*co*-S to BPMA-*co*-S was calculated from the slope of the curve as $k = 180\ \text{s}^{-1}$.

In this work, di(1-pyrenylmethyl)ether DiPyM was selected for monitoring the phototransformation of BZMA-*co*-S, since the fluorescence emission of DiPyM has been shown to be dependent on the cross-link densities of interpenetrating polymer networks [24]. DiPyM is a bichromophoric pyrene probe, where the chromophore is linked by a short chain. These types of probes exhibit dynamic excimer emission even at high dilution in low viscosity solution, and this emission may be supressed in high viscosity solutions or the solid phase, because the excimer formation depends on the possibility of the probes attaining the required conformation in their microenvironment.

Firstly, the UV absorbance of benzil (10^{-3} M) in methanol, in the absence and presence of a fluorescent probe (10^{-5} M) was measured, and it was found that the benzil absorption was not reduced by the DiPyM. These results indicate that irradiation of benzil groups are not influenced by the presence of the fluorescence probe, at least at the concentrations used in this work. Also, the fluorescence of DiPyM was analysed upon irradiation at λ > 400 nm, and no changes in the emission were observed, which confirms the photostability of the probe under the experimental conditions.

BZMA-*co*-S films doped with DIPyM were irradiated at λ > 400 nm and the phototransformation of the benzil groups was followed by FTIR spectroscopy. A similar behaviour was found for copolymer film doped with the fluorescence probe to that obtained for the reference without the fluorescent probe, confirming that the generation of benzoyl peroxide is not influenced by the presence of the probe.

The fluorescence emission of films of BZMA-*co*-S doped with DiPyM was analysed at different irradiation times. Fig. 3 illustrates

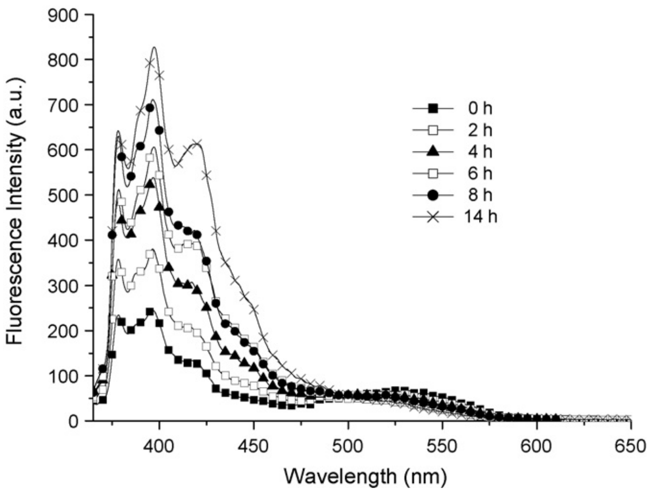

Fig. 3. Evolution of fluorescence emission spectra of DiPyM (λ_{exc} = 345 nm) upon irradiation at λ > 400 nm of BZMA-*co*-S film. [DiPyM] = 5 × 10^{-4} M.

the changes in the fluorescence spectra of the probe during irradiation.

In the fluorescence spectra, upon excitation at 345 nm, the unirradiated sample exhibited different emission bands. At lower wavelengths several resolved vibrational bands at 378, 390, 398 and 420 nm, were observed and can be assigned to monomer DiPyM emission as was found in other polymer matrices [3]. The spectra also exhibited another peak at 525 nm, which corresponded to the benzil group emission. In general, the fluorescence emission intensity at 525 nm decreased on irradiating the samples and became almost supressed at longer time periods. This behaviour corresponds to the disappearance of emitting species (1,2-dicarbonyl groups) and the subsequent generation of benzoyl peroxide. In addition, during irradiation the overall intensity of the emission at shorter wavelengths, corresponded to the increased fluorescence of the probe. This result may be associated with the reduced mobility of the probe in the copolymer, and this fact could be explained in terms of changes in free volume in the microenvironment of DiPyM. During irradiation the cross-linking of BZMA-*co*-S progressed, as was reflected by the increase in the molecular weight and increasing insoluble fraction in THF. Hence, the mobility of probe diminished and may cause a modification of the relaxation mode in the fluorescent probe. At longer times, when polymer crosslinking takes place, the free volume of the medium decreases, and rotational movements in the probe are highly hindered. As a consequence, the non-radiative processes are less favoured and radiative deactivation of the fluorescent probe from its singlet excited state is the favoured pathway. Therefore, an increase in fluorescence should be observed under these conditions. In addition, the fluorescence measurements during photoperoxidation of the benzil moieties in the presence of DiPYM under excitation at 345 nm may involve other reactions i.e. decreasing the benzil group concentration (bleaching) significantly would increase the amount of excitation light absorbed by DiPYM, which can lead to an increase in the DiPYM emission intensity.

The results obtained are in good agreement with the results obtained by FTIR spectroscopy. Fig. 4 shows the variation of fluorescence intensity at the maxima and the absorbance at 1678 cm^{-1} with time, revealing the usefulness of the fluorescence method for studying crosslinking processes in polymers.

Secondly, samples of irradiated BPMA-*co*-S copolymer films were thermally treated in an oven at 91 °C, and the thermal decomposition of photochemically generated peroxides was followed by FTIR spectroscopy and fluorescence analysis. In Fig. 5a, the FTIR spectra of BPMA-*co*-S upon thermal treatment at different times are shown. During the thermal decomposition of BPMA-*co*-S, the peroxide group depletion was followed by a decrease in the peroxide absorbance at 1764 cm^{-1}. This reaction was also accompanied by the increase in absorbances at 1735 and 1688 cm^{-1}, which corresponded to the generation of ester groups and benzoic acids.

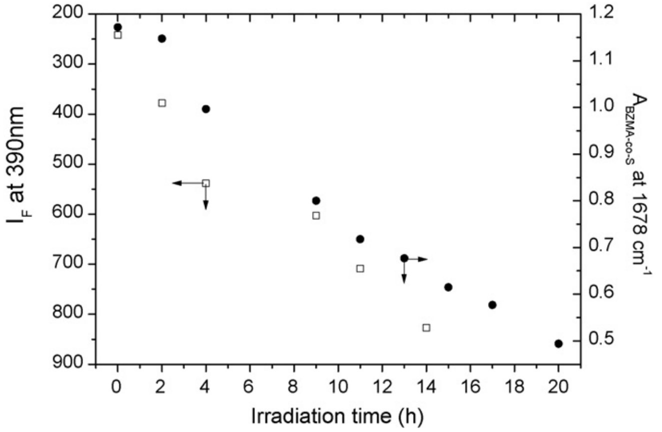

Fig. 4. Dependence of fluorescence emission intensity of DiPyM, and benzil absorbance at 1678 cm^{-1} upon irradiation of BZMA-*co*-S film at $\lambda > 400$ nm.

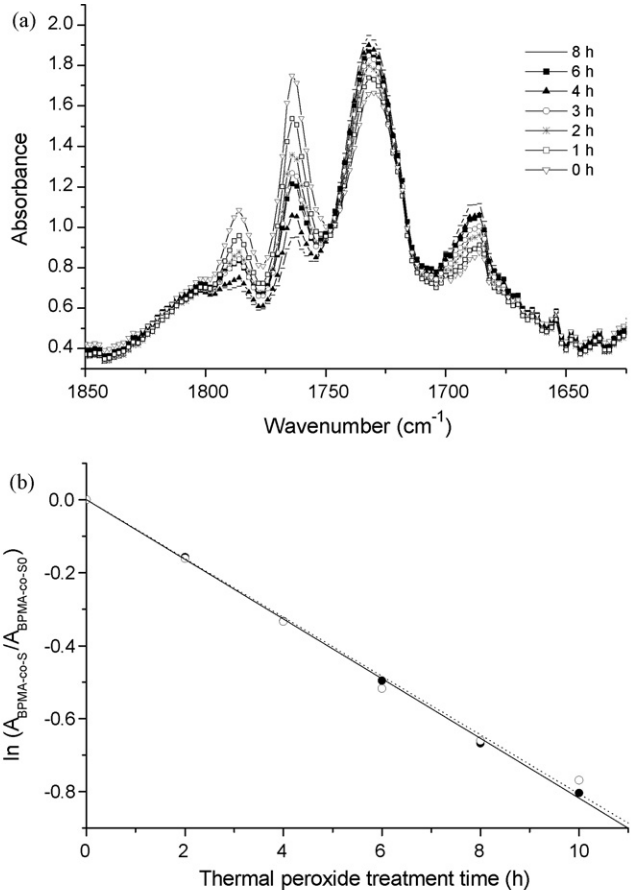

Fig. 5. Thermal decomposition at 91° C of BPMA-*co*-S film. (a) FTIR spectra at different times. (b) Rate of peroxide depletion at 1764 cm^{-1} in the absence (●) and presence (○) of DiPyM.

Analogous thermal treatment was undertaken for irradiated BPMA-*co*-S films doped with DiPyM and followed by FTIR spectroscopy. A plot of the thermal decomposition of BPMA-*co*-S in the presence and absence of the fluorescence probe versus time is shown in Fig. 5b. The rate constant of decomposition of BPMA-*co*-S was calculated from the slope of the curve, and a similar value ($k = 240\ \text{s}^{-1}$) was found for the doped sample with respect to that obtained in the absence of the probe.

Thermal decomposition of the BPMA-*co*-S polymer film doped with DiPyM was also monitored by fluorescence spectroscopy. For this purpose, the sample was heated at 91 °C in the oven chamber with air circulation, and the fluorescence spectra recorded at different times. As already mentioned, the fluorescence spectra of the irradiated sample BPMA-*co*-S exhibited several resolved vibrational bands corresponding to the fluorescent probe. An abrupt decrease in the fluorescence intensity was observed after 2 h of thermal treatment, and after 8 h, all the emission bands were highly reduced. In order to explain the decreasing fluorescence intensity during the decomposition of the benzoyl peroxide structures and crosslink formation by physical or chemical changes of the matrix, the presence of DiPYM in irradiated and thermally treated material was examined. For this purpose, the film was extracted by toluene and the fluorescence spectra of the extract measured. The spectrum

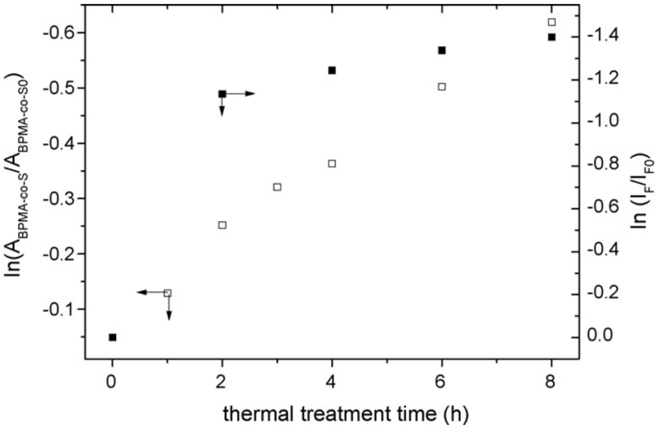

Fig. 6. Dependence of fluorescence emission intensity of DiPyM, and benzyl peroxide group absorbance at 1764 cm^{-1} upon thermal treatment at 91 °C.

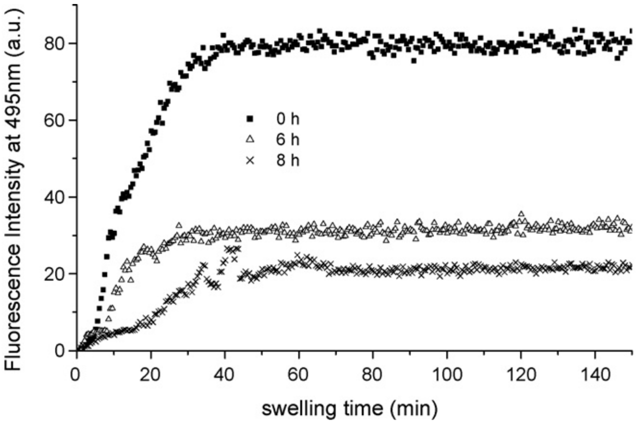

Fig. 7. Fluorescence intensity of DiPyM extracted from copolymer with different croslinking degree (irradiated and thermally treated at 0, 6, and 8 h), versus swelling time in cyclohexane.

is composed of structured monomer and broadband excimer emission. Since in solution only excimer emission of DiPYM should be observed, it would indicate that part of the DiPYM, on one pyrene structure or on a methylene group was changed, and such changes in the structure of DiPYM are probably not favourable for excimer formation. Different arguments might be put forward such as (i) the aromatic system would be attacked by benzoyloxy radicals during the formation of benzoyloxy pyrene structures, or (ii) the abstraction of a hydrogen atom from etheric methylene group by a benzoyloxy radical. Otherwise, the formation of oxidation products (peroxide, etc.) able to quench the excited states of emitting fluorophores may be considered [11]. The comparison between fluorescence and FTIR measurements upon thermal treatment are shown in Fig. 6.

3.2. Monitoring of swelling by real time fluorescence spectroscopy

It is well described in the literature [30,31], that DiPyM exhibits monomer emission in polymers below their Tg and contrary to that behaviour, the probe shows a broad excimer emission at 495 nm in solvents such as toluene or cyclohexane. In this work, this behaviour has been used to follow the diffusion of cyclohexane to the copolymer containing DiPyM, as a function of the crosslinking. The rate of extraction of the probe, as a consequence of swelling, has been monitored by the formation of excimer in the solvent. It may be expected to be dependent on the crosslinking of the material, since the solvents penetrate into the polymers with different rates depending on the density of the network.

Swelling of the polymer by cyclohexane was performed in the quartz cell of a spectrofluorimenter at 30 °C, and the formation of excimer was monitored by measurement of the fluorescence intensity at 495 nm during swelling time. The rate and intensity of excimer formation were determined for irradiated samples and those thermally treated at 91 °C, Fig. 7.

Initially, no excimer emission was observed for all the samples, which would confirm that a large volume for free rotational movements is required by DiPyM to lead to excimer formation. In the copolymers, all rotational movements are restricted, therefore, no excimer is observed. In general, the excimer emission intensity increased with swelling time, although some differences were observed for different cross-link densities that developed with time of thermal treatment. The rate of excimer emission formation is proportional to the concentration of the probe. To eliminate such a dependence on the probe concentration the calculation of the diffusion coefficients according to Eq. (2) is used [24,32] as a value responding to change in crosslink density.

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{15}\frac{1}{(2n+1)^2}\,e^{-D(2n+1)^2\pi^2 t/l^2} \qquad (2)$$

In this equation, the ratio of DiPyM groups extracted at time = t and time = 0, C_t/C_0, can be expressed in terms of fluorescence intensities $(I_t - I_\infty)/(I_0 - I_\infty) = C_t/C_0$ (where I_0, I_t and I_∞ are intensities after immersion of the film in cyclohexane solution for times 0 and t, and when the intensity increases incrementally by <1% during a 30 min period, respectively); l is the film thickness and D is a diffusion coefficient. The observed diffusion coefficients are presented in Table 1.

The rate of extraction and maximum fluorescence intensity obtained clearly showed that for an untreated sample (0 h), a larger free volume is available for the probe, associated with a lower degree of crosslinking. These samples are swollen faster and allow the probe to be more quickly extracted, in contrast to longer treatment times (6 and 8 h), where lower excimer formation was observed as a result of the higher hindrance for relaxation of the segments during swelling, and for instance, a slower extraction of DiPyM due to its entrapment in the network.

3.3. Chemiluminescence analysis during generation and decomposition of benzoyl peroxide carbonyl groups

The chemiluminescence temperature-ramping tests under nitrogen for initial BzMA-*co*-S and irradiated at different times were undertaken. The chemiluminescence profiles versus irradiation time are shown in Fig. 8. The unirradiated sample exhibited a very low intensity of chemiluminescence emission in the whole temperature range examined. Since in the absence of oxygen, the chemiluminescence in polymers is related to the initial concentration of hydroperoxide content generated during the processing of the material [33], it would indicate that no significant amounts of chemiluminescence species were induced by oxidation during film processing. The emission of chemiluminescence increases

Table 1
Diffusion coefficients of DiPYM upon various time of BPMA-*co*-S copolymer thermal treatment at 91 °C

Thermal treatment time (h)	D × 10^{12} (cm^2/s)	χ^2
0	7.83	0.0061
6	7.73	0.0052
8	2.44	0.00647

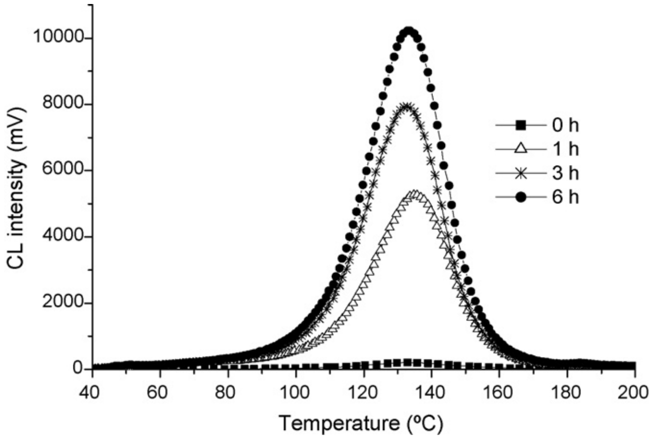

Fig. 8. Chemiluminescence temperature ramping curves under nitrogen atmosphere obtained for initial BzMA-*co*-S film and irradiated (λ > 400 nm) at different times.

above 95 °C, which corresponds to the region of the glass transition temperature of polystyrene. This transition involves motions of segments which favours the mobility of the peroxy radicals and their bimolecular termination reaction, responsible for the chemiluminescence emission in the polymers, through the deactivation of the generated carbonyl moieties in the excited state.

In general, chemiluminescence emission was enhanced with irradiation time. An abrupt increase in intensity was observed during the initial stages which can be related to the benzoyl peroxide moieties generated during irradiation. Benzoyloxy radicals are generated by thermal decomposition of benzoyl peroxide, and the recombination of benzoyloxy radicals or induced decomposition of benzoyl peroxide by benzoyloxy radicals would be responsible of chemiluminescence emission. A comparison between chemiluminescence and FTIR analysis evidenced the higher sensitivity of the former technique to be able to detect changes in the earlier stages of the phototransformation, Fig. 9. The increase of chemiluminescence intensity was interrupted at longer times of irradiation, when the concentration of those species tended to a nearly constant value. In this case, others factors may be considered to affect the chemiluminescence emission, such as the increasing crosslinking on irradiated samples, which would restrict the mobility of radicals to recombine due to the higher rigidity of the medium, or transfer reaction of benzoyloxy radicals on polymer matrix, which would decrease the chemiluminescence intensity.

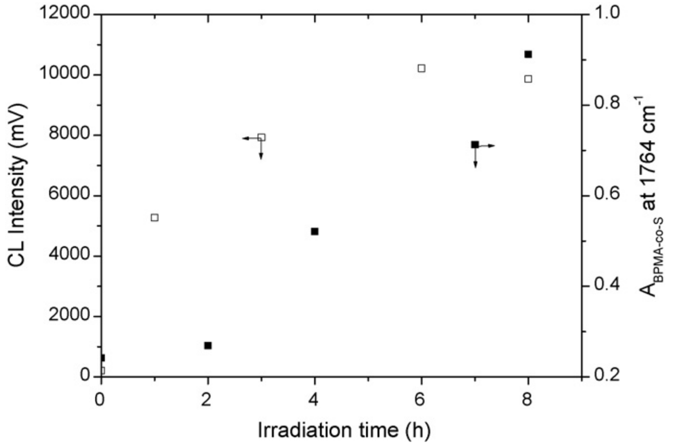

Fig. 9. Changes of BP groups absorption at 1764 cm^{-1} and CL maximum intensity upon various irradiation time at λ > 400 nm of BZMA-*co*-S polymer film.

Table 2
Kinetic data of chemiluminescence for BzMA-*co*-S, at 100 °C under nitrogen, after UV-irradiation at different times

Time (h)	$I_{\text{CL-max}}$ (mV)	$A_{\text{CL-peak}}$ (mV) × 10^{-3}	CL decay rate × 10^4 (mV$^{-1/2}$ min^{-1})
0	104	10	5.12
2	2339	214	0.73
6	2832	248	0.78
12	3304	286	0.64

The behaviour described for irradiated copolymers is evidenced by an analysis of the films in isothermal chemiluminescence experiments under nitrogen. The isothermal chemiluminescence analysis under nitrogen at 100 °C was undertaken for all copolymer films. The obtained results are plotted in Fig. 10, and the chemiluminescence parameters, CL-decay rate, $I_{\text{CL-max}}$ and $A_{\text{CL-peak}}$ shown in Table 2. The parameter CL-decay rate was calculated from the slope of the reciprocal of the square root of the chemiluminescence intensity versus time [34]. This slope is defined as $\sqrt{k_b/f}$, where k_b is the bimolecular constant rate of the hydroperoxides decomposition.

As expected, the intensity of chemiluminescence and the area of the emission curve for unirradiated films were very low. An increase of CL emission was detected for those irradiated films when compared with the initial sample. A good correlation was seen between the chemiluminescence parameters. Higher values of the intensity

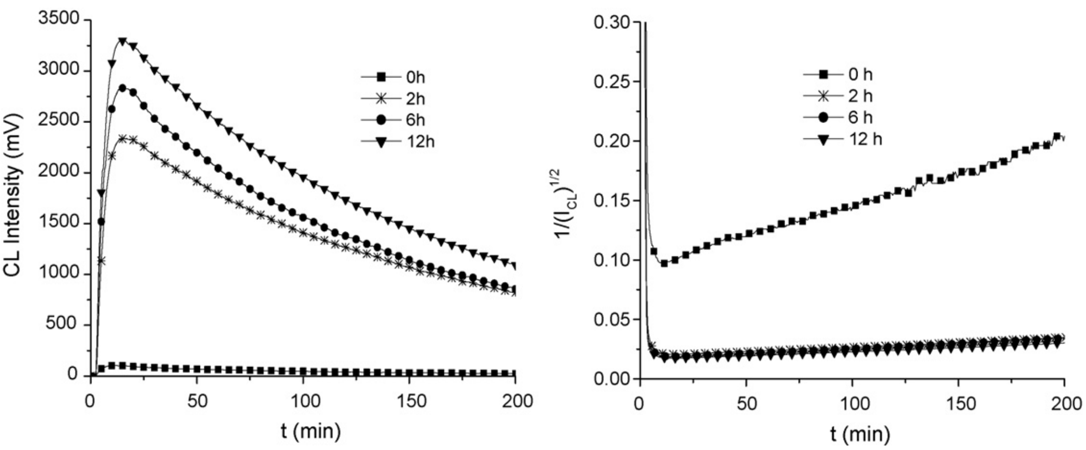

Fig. 10. (a) Chemiluminescence curves versus time (b) plot of the reciprocal of square root of chemiluminescence intensity versus time, obtained at 100 °C under nitrogen for BZMA-*co*-S film upon irradiation at λ > 400 nm at different times.

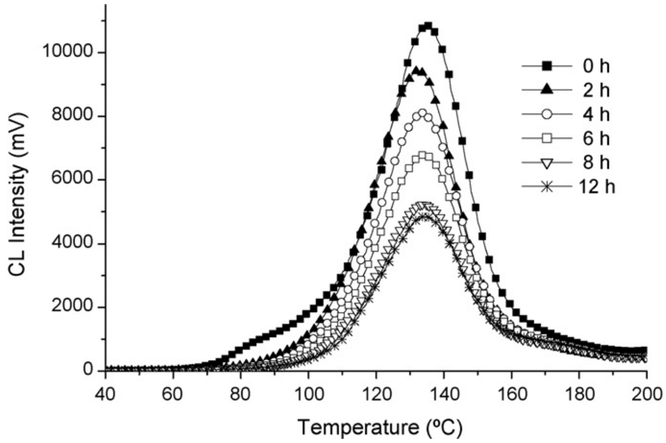

Fig. 11. Chemiluminescence temperature ramping curves under nitrogen atmosphere obtained for initial BPMA-*co*-S film and heated at 91 °C at different times.

of chemiluminescence in the peak-top ($I_{\text{CL-max}}$) and integrated area of CL-signal ($A_{\text{CL-peak}}$) with increasing the irradiating time were found, as was observed in the non-isothermal chemiluminescence analysis. Moreover the values of CL-decay rate decreased for the samples under UV-exposure, which corresponded to the higher rigidity of the medium associated with the higher cross-link densities in the irradiated samples thus, restricting the recombination of benzoyloxy radicals.

The emission of chemiluminescence versus temperature was measured for thermally treated films of BPMA-*co*-S, Fig. 11. Lower values of the intensity of chemiluminescence in the peak-top ($I_{\text{CL-max}}$) and integrated area of CL-signal ($A_{\text{CL-peak}}$) with increasing time were found. This fact may be associated with the thermal decomposition of photochemically generated peroxides, as was previously followed by FTIR spectroscopy, Fig. 12.

In previous work, chemiluminescence emission studies have been used to sense temperature-dependent morphological changes, i.e. annealing processes, and to determine relaxation temperatures and exothermic recrystallisation peaks [6,20]. In this paper a clear correlation is demonstrated between morphology and chemiluminescence emission properties. CL technique has been efficiently employed as a highly sensitive method that gives information on the crosslinking of the polymer material undergoing photochemical transformation processes.

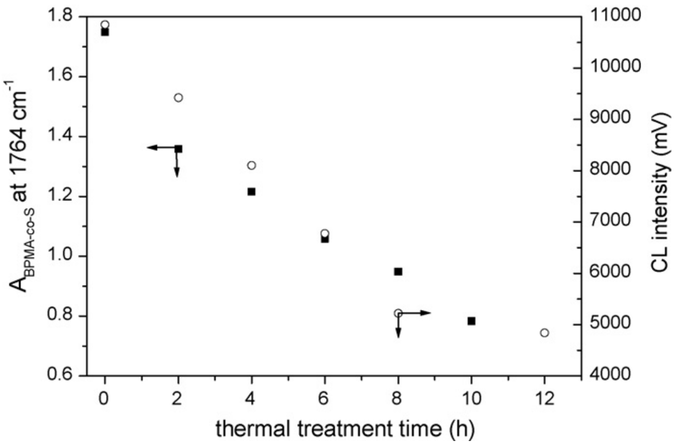

Fig. 12. Decrease of BP groups absorption at 1764 cm^{-1} and CL maximum intensity upon various time thermal decomposition of BPMAcoS polymer film at 91 °C.

4. Conclusions

Chemiluminescence emission has been used as a valuable method to analyse processes in polymers, such as the photochemical formation of benzoyl peroxide pendant groups in BZMA-*co*-S, and their thermal decomposition giving rise to crosslinking. In general, chemiluminescence emission was enhanced with irradiation time, which would is related to the generation of benzoyl peroxide moieties. The values of CL-decay rate decreased for the samples under UV-exposure, and this result may be associated with the higher rigidity of the medium in the irradiated samples, which restricts the recombination of benzoyloxy radicals. For thermally treated films of BPMA-*co*-S, the intensity of chemiluminescence was seen to decrease with time, which corresponded to the thermal decomposition of photochemically generated peroxides. These results are in accordance with those obtained by means of fluorescence analysis of an intramolecular excimer forming fluorescent probe, DiPyM.

These results contribute to the development of a sensitive chemiluminescence-based method in order to assess physical or chemical changes during the early stages of crosslinking. A good correlation was observed between fluorescence, FTIR and CL measurements during photochemical formation and thermal decomposition of peroxides. Therefore, it is possible to measure the rate of photocrosslinking of a material by the chemiluminescence method after a very short time of exposure due to its sensitivity compared to that of fluorescence.

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