

“Luminescent polymers containing pyrenyl groups prepared by frontal polymerization of di(ethylene glycol) ethyl ether acrylate using Trigonox-23 as initiator”

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H I G H L I G H T S

- ▶ Thermal Frontal polymerization of DEGEAA acrylate was studied in detail.
- ▶ Trigonox-23 was used as initiator for the first time in frontal polymerization.
- ▶ This initiator prevents bubbling formation giving homogeneous pieces.
- ▶ Conversion, temperature profiles, front velocities were determined.
- ▶ First synthesis of luminescent polymers by frontal polymerization.

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Thermal frontal polymerization (FP) of di(ethylene glycol) ethyl ether acrylate (DEGEAA) was carried out using as radical initiator tert-butyl peroxyneodecanoate (Trigonox-23), which has not been previously employed in FP. The influence of the initiator concentration on the formation of the propagating front, the maximum reached temperature and the front velocity was studied in detail. The results were compared to those obtained in the bulk polymerization of this monomer. Furthermore, a pyrene containing monomer was incorporated as fluorescent probe in order to obtain luminescent materials with different chromophore contents. The resulting polymers were characterized by FTIR spectroscopy in the solid state. Their thermal properties were determined by differential scanning calorimetry (DSC), which was also used to calculate the conversion degree in the FP of DEGEAA at different initiator concentrations. Moreover, the optical properties of these materials were studied by absorption and fluorescence spectroscopy. The maximum amount of incorporated pyrene containing monomer in the polymer matrix was limited by its maximum solubility in DEGEAA (10% wt). The presence of an excimer emission band confirmed the presence of intermolecular pyrene–pyrene interactions.

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1. Introduction

Frontal polymerization (FP) is a relatively easy technique that converts a mixture of monomer and initiator into polymer by means of an external stimulus, mainly thermal or photochemical. This favours the formation of a polymerization front which propagates directionally through the reaction vessel. FP offers some advantages compared to other polymerization methods and can be also applied in “green chemistry”. Among these advantages we can mention that: a) no solvent is needed in the

polymerization mixture, b) the autpropagation reaction through the vessel generally guarantees almost total conversion of the monomer into polymer, and c) there is a low energy consumption because the external energy source is applied only for a short time [1].

There are some important factors to be considered in order to promote the formation and persistence of a propagating front in a free-radical FP. The monomer does not have to react at room temperature, and an initial energy input has to be provided in order to generate free radicals able to initiate the polymerization process. The conversion of monomer into polymer is highly exothermic and induces a self-propagating thermal reaction, which results in a boundary wave, separating the formed polymer from the liquid monomer. This exothermicity helps the propagating front to self-

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sustain, since the amount of released heat during the reaction has to be larger than that lost in the reaction zone. When the amount of generated heat is not high enough, a supplementary amount of energy has to be provided in order to induce the polymerization of the monomer close to the reaction zone, since FP takes advantage of the heat released in the reaction and its dispersion by thermal conduction [2]. Moreover, it is necessary to use monomers with elevated boiling points in order to prevent bubble formation, which may result from the high temperature reached by the travelling front [3].

The first studies on frontal polymerization were performed by Chechilo et al. who polymerized methyl methacrylate (MMA) under high pressure conditions (>3000 atm) [3,4]. They studied the effects of pressure and initiator concentration over the propagating front rate. Since this early work, FP has attracted the attention of many research groups which got involved in this research field. Davtyan et al. studied the gel effect on the frontal radical polymerization of MMA [5]. On the other hand, Pojman et al. carried out FP studies on acrylic monomers [4,6,7], epoxy resins [8,9], and urethane-acrylates [10]. They also investigated the formation of simultaneous-interpenetrating polymer networks [11], the influence of the reactor geometry, the spin modes [8], and the use of a micro-encapsulated initiator [9,12]. Mariani et al. employed FP to prepare unsaturated polyester/styrene resins [13], diurethane acrylates [14], and different kinds of hydrogels [15–18]. Chen et al. achieved the FP of vinylpyrrolidone [19], 2-hydroxyethyl acrylate [20], and N-methylolacrylamide [21]. Recently, we reported the copolymerization of poly(ethylene glycol) diacrylate (PEGDA) with the (E)-2-(ethyl(4-((4-nitrophenyl)diazanyl)phenyl)amino)ethyl methacrylate (MDR-1) via FP using BPO as initiator [22]. PEGDA has been employed in biomaterials science for the elaboration of phase-separation membranes for proteins, as adsorbent of metallic ions in different kinds of solutions, in drug delivery applications, and in the preparation of hydrogels able to respond to external stimuli such as pH or temperature [23,24]. Similarly, we reported the FP of 2-phenoxyethoxyacrylate (2-PEA) and its copolymerization with MDR-1 using two ionic liquids as initiators: tetrabutylphosphonium persulfate (TBPPS) and trihexyltetradecylphosphonium persulfate (TETDPPS) [25]. A great advantage of FP is its ability to convert *in situ*, rapidly and uniformly, a monomer or mixture of monomers into polymer [26].

On the other hand, acrylic monomers bearing short poly(ethylene)glycol (PEG) segments are versatile building-block agents for the preparation of “smart” bio-relevant materials, because non end-capped poly(ethylene glycol) ether moieties make them amphiphilic or compatible with both polar and non-polar solvents [27,28]. Therefore, PEG derivatives are used as diluents and leveling agents in the manufacture of paints, baking finishes, in the fabrication of nitrocellulose, for combination of lacquers and additives [27,28]. Many PEG containing monomers are commercial and can be polymerized either by anionic, radical or living radical polymerization. Particularly, di(ethylene glycol) ethyl ether acrylate (DEGEEA) has been widely employed for the preparation of pressure sensitive adhesives, chemical intermediates, metal and paper coatings, PVC floor, wood coatings, inks and paints [29]. A very common problem with coatings is that sometimes they crack during the drying process. That is why FP can be a good alternative to overcome this problem.

Regarding pyrene, this compound has been considered an efficient fluorescent probe and has been successfully used as a molecular label in the study of a large variety of polymers [30–33,35]. It is very well known that pyrene has a long singlet lifetime and readily forms excimers. The most relevant aspects of the photophysics of pyrene containing polymers have been the subject of some reviews [34,35]. In the last 10 years our research group has incorporated

pyrene into different polymers and well-defined oligomers, in order to study by absorption and fluorescence spectroscopy the influence of the geometry of the molecule, the internal stacking and the pyrene–pyrene distance on the optical properties of these compounds [36–40].

Herein, we report for the first time the thermal FP of DEGEEA using tert-butyl peroxyneodecanoate (Trigonox-23) as radical initiator. We investigated the influence of initiator concentration on the front velocity (V_f), maximum temperature (T_{max}), conversion degree and temperature profiles. Moreover, the results were compared to those obtained by classical bulk polymerization and in the FP of DEGEEA using benzoyl peroxide (BPO) as initiator. After having determined the optimal conditions for the FP of DEGEEA, we performed the copolymerization of this monomer in the presence of 1-pyrenylbutyl acrylate (PyBuAc) in order to obtain light emitting polymers. These materials were characterized by FTIR spectroscopy, and their thermal properties were evaluated by Differential Scanning Calorimetry (DSC). Finally, their optical properties were studied by absorption and fluorescence spectroscopy in the solid state. The polymerization of DEGEEA and its copolymerization with PyBuAc are illustrated in Fig. 1.

2. Experimental part

2.1. Materials

DEGEEA (FW = 188.22 g mol⁻¹, d = 1.016 g mL⁻¹, bp = 95 °C) and BPO (FW = 242.23 g mol⁻¹, mp = 102–105 °C) were purchased from Sigma–Aldrich. Trigonox-23 (FW = 244.4 g mol⁻¹, d = 0.877 g mL⁻¹) was purchased from AkzoNobel. All compounds were used as received without further purification.

2.2. Synthesis of 1-pyrenylbutyl acrylate

1-Pyrenylbutanol (2 g, 7.289 mmol) was dissolved in freshly distilled THF (50 mL) under argon atmosphere; then triethylamine (1.5 mL, 10.6 mmol) was added with a syringe to the solution. The

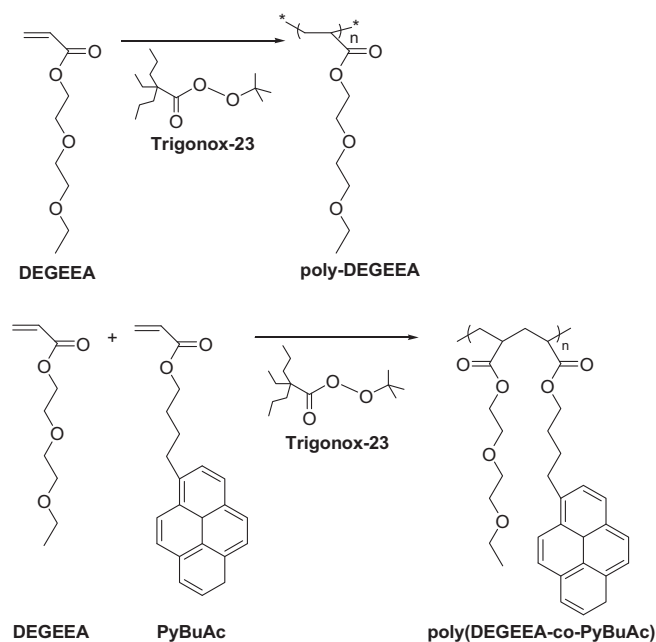


Fig. 1. Polymerization of DEGEEA and its copolymerization with 1-pyrenylbutyl acrylate.

mixture was cooled in an ice bath and acryloyl chloride (0.713 mL, 8.823 mmol) dissolved in THF (5 mL) was added dropwise by means of an addition funnel. The reaction mixture was stirred for 24 h at room temperature. The resulting product was extracted with chloroform, dried with anhydrous MgSO_4 and concentrated at reduced pressure. Then, the crude product was purified by flash column chromatography on silica gel, using a mixture hexane-chloroform 50:50 as eluent. 1-pyrenylbutyl acrylate was obtained as a pale yellow solid. Yield: 53%. FTIR (KBr): $\nu = 3090$ (s, C–H aromatic and vinylic), 2961 (s, CH_2), 1727 (s, C=O), 1603 (s, C=C aromatic), 1337 (s, C–O of the ester), 1100 (s, O– CH_2), 852 (out of plane, $=\text{CH}_2$ aromatic), 802 (out of plane, $=\text{C–H}$ vinylic) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) (Scheme 1): $\delta = 8.28$ – 7.26 (m, 9H, aromatic protons H^4 – H^{12}), 6.44 (d, 1H, H^2), 6.14 (dd, 1H, H^3), 5.82 (d, 1H, H^1), 4.25 (t, 2H, OCH_2), 3.40 (t, 2H, O– CH_2 – CH_2), 1.97 (t, 2H, Py– CH_2) and 1.86 (t, 2H, Py– CH_2 – CH_2) ppm. ^{13}C NMR (CDCl_3 , 100 MHz) (Scheme 1): $\delta = 166.62$ (1C, C^{e}), 136.50, 131.64, 131.09, 130.83 (4C, aromatic carbons), 130.08 (1C, C^{g}), 128.82, 128.73 (2C, aromatic carbons), 127.70 (1C, C^{f}), 127.49, 127.42, 126.85, 126.03, 125.31, 125.22, 125.10, 125.01, 124.92, 123.47 (10C, aromatic carbons), 64.58 (1C, C^{d}), 33.23 (1C, C^{a}), 28.82 (1C, C^{c}), 28.29 (1C, C^{b}) ppm.

2.3. Frontal polymerization experiments

In a glass test tube (16 cm length, 16 mm inner diameter), DEGEAA (5 mL, 28.258 mmol) monomer and the appropriate amount of initiator (Trigonox-23 or BPO, Table 1) were mixed together at room temperature until the initiator was completely dissolved. Different initiator concentrations were used: 0.5, 1.0, 1.5, 2.0, 5.0 and 10% wt with respect to that of DEGEAA. Then, the test tubes were locally heated at the top level of the solution, using a soldering iron as heating source, until the formation of a propagating front was observed. The heat released during the conversion of the monomer into polymer was responsible for the formation of a hot polymerization front, able to self-sustain, and propagate throughout the whole tube. V_f were calculated by measuring the distance recorded by the front in a given time and were expressed in centimetres per minute (cm min^{-1}). The labelled polymers were synthesized similarly, using the required amounts of DEGEAA and 1-pyrenylbutyl acrylate.

Temperature profiles were determined using a J-type thermocouple placed into the monomer mixture at 1 cm (± 0.5 cm) from the bottom of the tube. It was connected to a digital scanning thermometer (Digi-Sense 69200-00) for temperature recording and reading. The position of the front, easily visible through the

Table 1

Conversion degree of DEGEAA, varying the Trigonox-23 concentration.

Trigonox-23 (wt. %)	Residual ΔH_r (J/g)	Total ΔH_t (J/g)	Degree of conversion (%)	T_g ($^{\circ}\text{C}$)
0.25	–1.02	–391.8	99.7	–60
0.5	–0.19	–267.3	99.9	–65
1	–0.03	–318.5	99.9	–64
1.5	–0.04	–405.6	99.9	–68
2	–0.08	–408.1	99.9	–72
5	–0.01	–406.1	99.9	–70
10	–0.07	–446.1	99.9	–68

glass walls of the tube, was measured as function of the time. The formed polymers were removed from the test tubes and analysed by DSC in order to determine their conversion degree and glass transition temperature (T_g). In the case of the labelled polymers, the samples were powdered and purified by soxhlet extraction with methanol in order to remove traces of remaining 1-pyrenylbutyl acrylate.

2.4. Bulk polymerization experiments

In a glass test tube (16 cm length, 16 mm inner diameter), adequate amounts of DEGEAA monomer and initiator (Trigonox-23) were mixed together at room temperature, until all the reagents were mixed. Different Trigonox-23 concentrations were used: 0.5, 1.0 and 2.0% wt. with respect to that of DEGEAA. Then, the tubes containing the mixture were immersed and heated in an oil bath at 60°C . The polymerization reaction was monitored by TLC until it was completed after 3 h.

2.5. Characterization of the labelled monomer and the obtained polymers

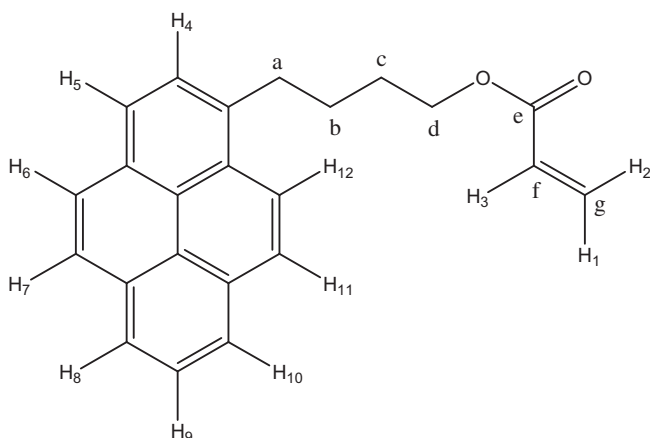
The FTIR spectra of the monomers and the corresponding polymers were recorded on a Spectrum 100 (Perkin Elmer PRECISELY) spectrometer in KBr pressed pellet for the labelled monomer and the formed polymers, and in thin film for the DEGEAA monomer. Polymerization of the samples was confirmed by comparing the FTIR spectra of polymers with those of the monomers. ^1H and ^{13}C NMR spectra of the labelled monomer in CDCl_3 solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer, operating at 400 MHz and 100 MHz for ^1H and ^{13}C , respectively.

Thermal properties of the obtained polymers were studied by determining the T_g . DSC measurements were conducted in a DSC 2910 TA Instrument. For each sample, two consecutive scans were carried out from -85 – 150°C with a heating rate of $5^{\circ}\text{C min}^{-1}$, under nitrogen atmosphere. Monomer conversion and T_g values were determined from the first thermal scan. In all cases, the conversion was almost quantitative and was calculated by the following equation:

$$(\%) = [1 - (\Delta H_r / \Delta H_t)] \cdot 100$$

Where ΔH_r (residual) is the peak area obtained for the residual polymerization after the first thermal scan, and ΔH_t (total) is the area under the curve when the polymerization was carried out in the DSC instrument.

Polymer films were prepared by polymerizing mixtures containing the appropriate amounts of monomer, labelled monomer and initiator, deposited on a quartz substrate. All samples were heated for 3 h at 60°C in a hot plate.



Scheme 1.

Absorption and fluorescence spectra of the labelled monomer were recorded in THF (spectrophotometric grade), which was purchased from Aldrich. Prior to use, this solvent was checked for spurious emission in the region of interest and was found to be satisfactory. The absorption spectra were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer (model 8452A) in film for the polymers, and in solution for the labelled monomer (concentration 10^{-5} M), using a 1 cm quartz cell. It has been verified that the Beer–Lambert law applies for such concentration.

Fluorescence spectra corrected for emission detection were recorded on a Fluorolog-3 spectrophotometer with an FL3-11 special configuration, which is designed to record simultaneously two emission scans (T-shape). Pyrene containing monomer solution (concentration 10^{-6} M) was excited at the maximum absorption wavelength $\lambda = 345$ nm. For labelled polymers, emission spectra were recorded in film exciting at the same wavelength.

3. Results and discussion

3.1. Frontal polymerization of DEGEAA

Thermal frontal polymerization of DEGEAA was carried out in a test tube under different reaction conditions, using the tip of a soldering iron as heating source. First, we performed the polymerization reaction, varying the amount of initiator (Trigonox-23). Fig. 2 shows the data of the front position as a function of time for the FP of DEGEAA with 0.25, 1.5 and 10% wt. of Trigonox-23. From this figure, it can be seen that front velocity increases as the initiator concentration augments.

According to Fig. 2, we can notice that FP exclusively occurred since in all cases the front velocity increases linearly as a function of time. In fact no deviations from linearity were observed, which reveals that no undesired spontaneous polymerization takes place.

When Trigonox-23 is used as radical initiator, well defined homogeneous fronts are observed. On the other side, with BPO the formation of bubbles occurs during the FP process which affects the morphology of the resulting polymer, giving porous and heterogeneous samples with cracks and defaults. Unfortunately, front velocities in the FP of DEGEAA are very difficult to determine when BPO is used as initiator, because of the formation of bubbles.

On the other hand, T_{\max} was measured for the different experiments as a function of initiator concentration. The temperature

profiles for the FP of DEGEAA using different concentrations of Trigonox-23 are shown in Fig. 3. According to these profiles, an increase in temperature was observed in the range between 200 and 500 s for all samples. The horizontal part of the curves of T_{\max} confirms again the occurrence of a pure FP process. As it was expected, the highest value of T_{\max} was observed for the sample obtained with the maximum initiator concentration (Fig. 3).

On the other hand, the influence of the amount of Trigonox-23 on the V_f was also studied employing concentrations from 0.5 to 10 % wt. (Fig. 4). As it can be noticed, V_f increases with the amount of initiator. Nevertheless, when concentrations beyond 5% wt. of Trigonox-23 were used, a stationary state was reached with a maximum V_f value of 0.0425 cm s^{-1} or 2.55 cm min^{-1} .

T_{\max} of the samples was monitored as a function of the initiator concentration (Fig. 5). As it was expected, T_{\max} increases as the initiator concentration augments. However, a decrease in T_{\max} was observed when amounts higher than 5% wt. of Trigonox-23 were employed.

T_g of the poly(DEGEAA) samples were determined and analysed as a function of the initiator concentration (Table 1). As it can be seen, T_g values of the polymers did not vary significantly, ranging between -70 and -60 °C, showing a slight decrease at higher initiator concentrations. This is mainly due to the lower viscosity and molecular weights of the obtained polymers.

Finally, all samples were analysed by DSC and it was found that conversions were almost quantitative with values ranging from 99.7 to 99.9%. The total enthalpy (ΔH_t) and maximum temperature (T_{\max}) were obtained from the first thermal scan, whereas the values of remaining enthalpy (ΔH_r) and its associated maximum temperature (T_2) were determined from the second thermal scan. The obtained results are summarized in Table 1. The conversion values observed with Trigonox-23 using low initiator concentrations were compared to those obtained with BPO, and the results are shown in Table 2.

As it can be noticed, the conversion values obtained with Trigonox-23 are higher than those obtained with BPO initiator.

FTIR spectra of DEGEAA and poly(DEGEAA) were recorded and are shown in Fig. 6. If we analyse the spectrum of DEGEAA (Fig. 6a), we can observe a series of bands at 2979, 2868 (CH_2), 1719 ($\text{C}=\text{O}$), 1635 ($\text{C}=\text{C}$), 1292 ($\text{C}-\text{O}$ ester), 1189, 1109, 1061 ($\text{C}-\text{O}$ ethers) and 982 ($=\text{C}-\text{H}$, out of plane) cm^{-1} . In the FTIR spectrum of poly(DEGEAA) (Fig. 6b) the band at 1635 cm^{-1} due to $\text{C}=\text{C}$ group decreases remarkably in intensity with respect to that observed in the FTIR

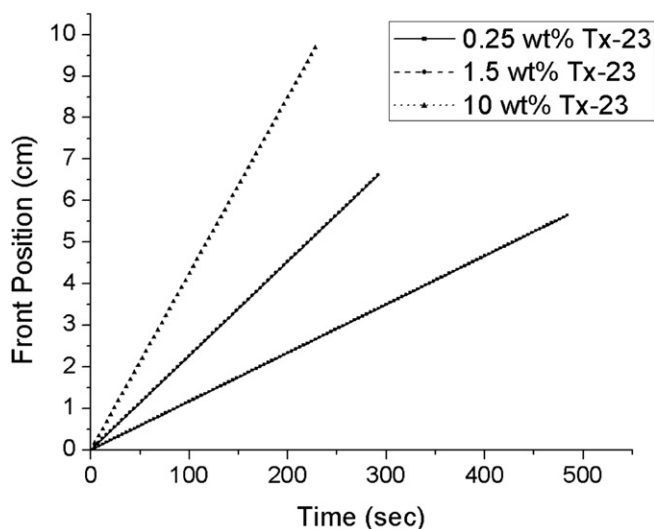


Fig. 2. Front position vs. time for the FP of DEGEAA using 0.25, 1.5, and 10% wt. of Trigonox-23.

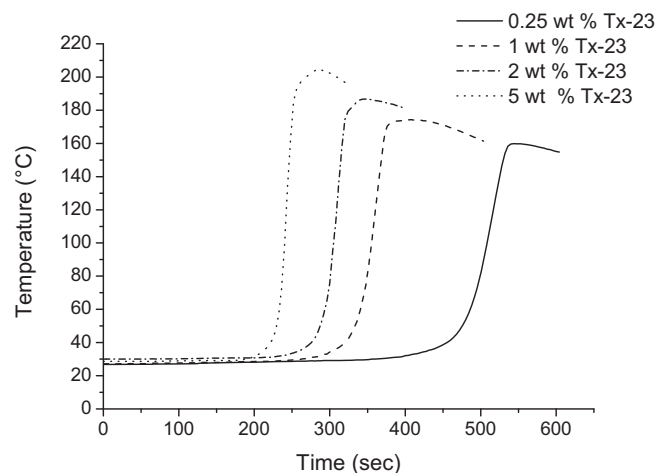


Fig. 3. Temperature profiles (temperature vs. time) for the FP of DEGEAA at different Trigonox-23 concentrations (0.5, 1, 2 and 5% wt.).

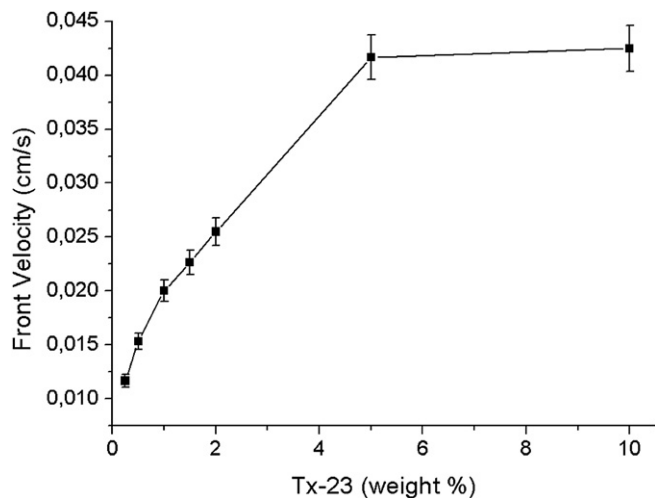


Fig. 4. Front velocity vs. initiator concentration for the FP of DEGEEA, using 0.25, 0.5, 1, 1.5, 2, 5 and 10% wt. of Trigonox-23.

spectrum of DEGEEA, which confirms that FP occurred. Moreover, in the poly(DEGEEA) spectrum the band at 1292 (s, C–O ester) is less intense, and a broad band is observed at 1105 cm^{-1} due to the C–O groups present in the di(ethylene glycol) segments.

3.2. Preparation of luminescent polymers containing pyrene

We carried out the copolymerization of DEGEEA monomer in the presence of PyBuAc. Different amounts of PyBuAc were used: 1, 2, 5 and 10% wt, keeping the Trigonox-23 concentration equal to 5% wt. The obtention of the labelled polymers was confirmed by FTIR spectroscopy (Fig. 6c). The prominent bands at 852 and 708 cm^{-1} (=C–H aromatic, out of plane) indicate that the pyrene containing monomer was successfully incorporated into the polymer backbone.

3.3. Optical properties of the polymers

Since polymers obtained by FP and those obtained by bulk polymerization exhibit similar optical properties, polymer films

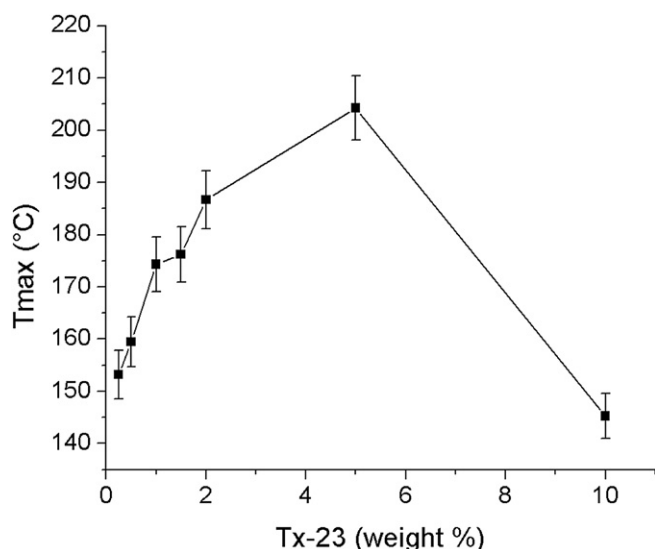


Fig. 5. T_{max} vs. initiator concentration for the FP of DEGEEA with Trigonox-23.

Table 2
Comparison between the PF of DEGEEA, using BPO vs Trigonox-23.

Initiator (wt. %)	Residual ΔH_f (J/g)	Total ΔH_f (J/g)	Conversion (%)	T _g (°C)
BPO (1%)	-68.52	-400.3	82.8	-57
Tx-23 (1%)	-0.03	-318.5	99.9	-64
BPO (2%)	-119	-413.6	71.2	-55
Tx-23 (2%)	-0.08	-408.1	99.9	-72

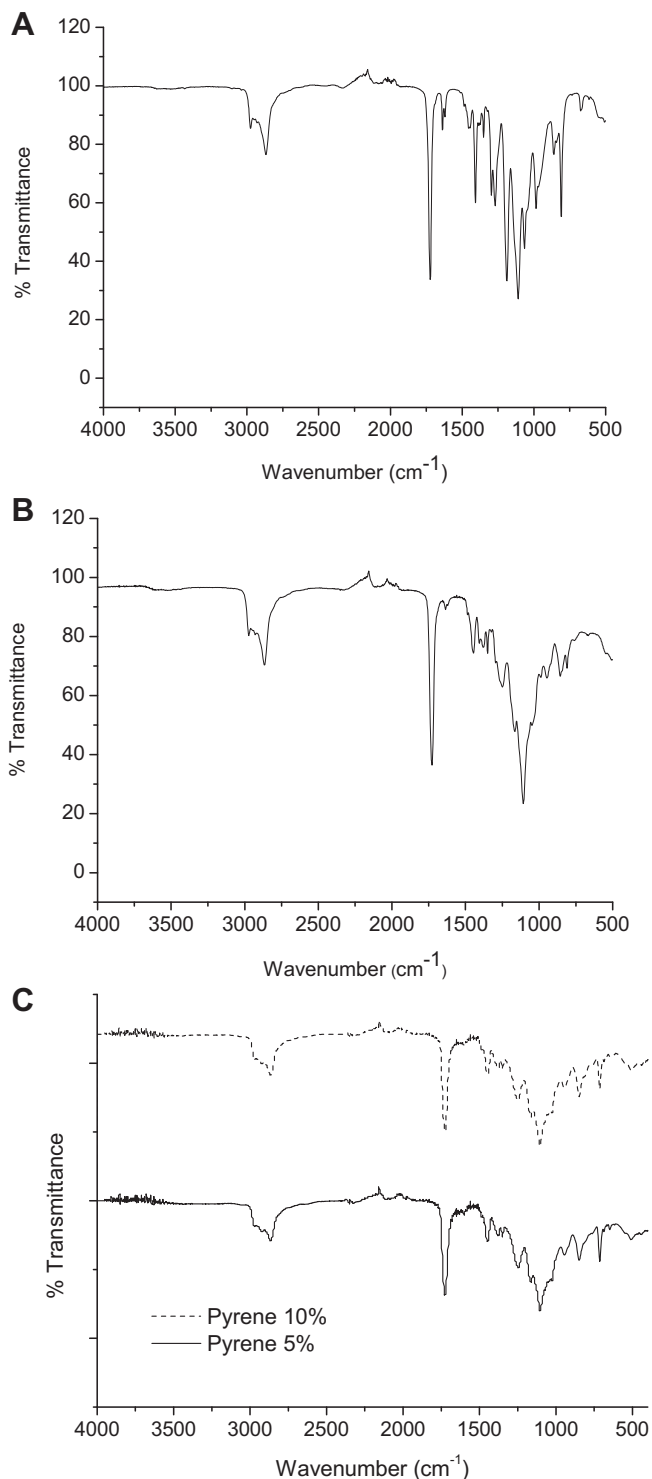


Fig. 6. FTIR spectra of a) DEGEEA monomer, b) poly(DEGEEA) and c) poly(DEGEEA-co-PyBuAc) (5 and 10% wt).

Table 3
Optical properties of the poly(DGEEA-co-PyBuAc) copolymers.

Polymer	Absorption λ_{\max} (nm)	Monomer emission λ_M (nm)	Excimer emission λ_E (nm)	I_M/I_E
poly(DGEEA-co-PyBM) 1% pyrene	345	377–398	—	—
poly(DGEEA-co-PyBM) 2% pyrene	345	377–398	485	4.82
poly(DGEEA-co-PyBM) 5% pyrene	ND	402–423	495	1.70
poly(DGEEA-co-PyBM) 10% pyrene	ND	402–423	495	1.57

ND. Not determined because of saturation.

were prepared by polymerizing mixtures with the appropriate ratio (monomer/labelled monomer/initiator) deposited on a quartz substrate. The optical properties of the copolymers were studied by absorption and fluorescence spectroscopy and the results are summarized in Table 3. Besides, the normalized absorption spectra of the PyBuAc monomer in THF solution and those of the poly(DGEEA-co-PyBuAc) copolymers in film are shown in Fig. 7.

As we can see PyBuAc monomer (Fig. 7a) exhibits a well defined structured band at $\lambda = 345$ nm, due to the $S_0 \rightarrow S_2$ transition of pyrene. In the absorption spectra of the poly(DGEEA-co-PyBuAc) copolymers (Fig. 7b), this band is also observed but it suffers a significant broadening due to the high content of the pyrene

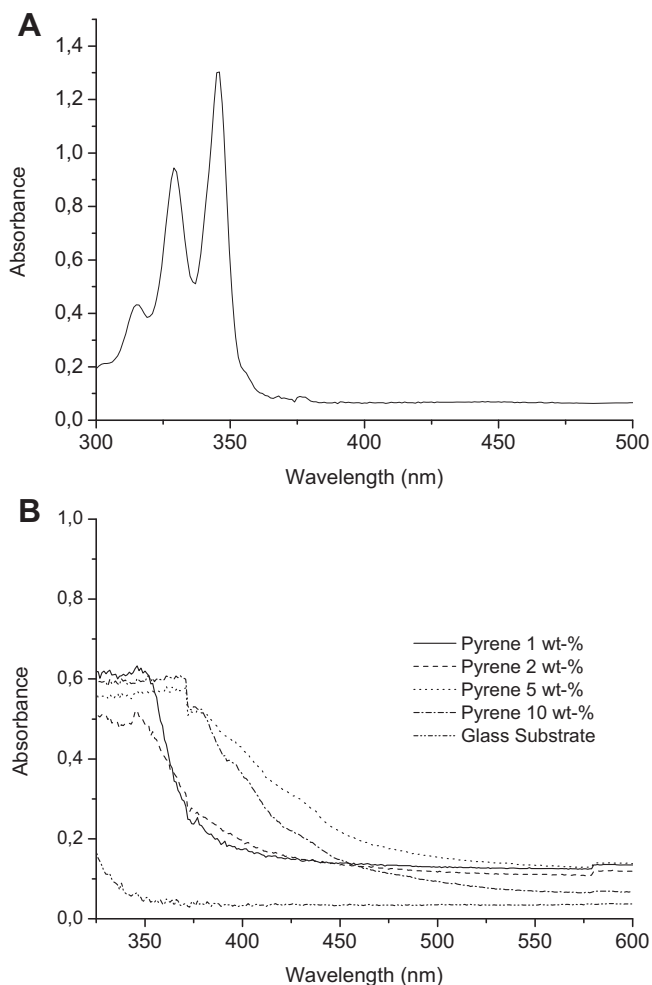


Fig. 7. Absorption spectra of a) PyBuAc monomer and b) poly(DGEEA-co-PyBuAc) copolymers.

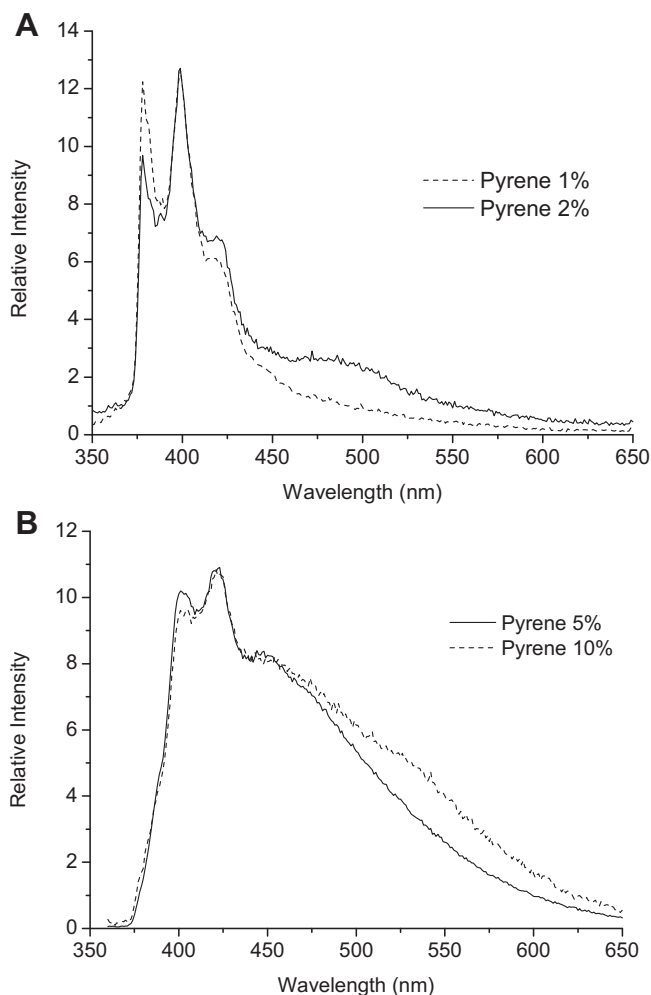


Fig. 8. Fluorescence spectra of poly(DGEEA-co-PyBuAc) copolymers: a) 1 and 2% wt. pyrene, b) 5 and 10% wt. pyrene.

chromophore which gives rise to pyrene–pyrene interactions. According to Winnik [34], if the intensities ratio between the peak (I_p) and the valley (I_v) of this band is $I_p/I_v < 3$, there is pre-association of the pyrene chromophores in the ground state. This rule applies for pyrene containing polymers in solution. Since the polymers were analysed in the solid state, in samples bearing the highest pyrene content (5 and 10%) a saturation of this band is observed. Nevertheless, with lower concentrations (1 and 2%) we can see a structured absorption band.

On the other hand, fluorescence spectra of the labelled polymers with different pyrene contents were recorded in thin films at room temperature, exciting at $\lambda = 345$ nm (Fig. 8).

As it can be seen, poly(DGEEA-co-PyBuAc) copolymers bearing 1 and 2% wt. pyrene content (Fig. 8a) exhibit a well-defined band at $\lambda_M = 377$ –398 nm, arising from excited pyrenes in the non-associated state or “monomer emission”. However, samples bearing higher content of this chromophore showed also an excimer emission band at $\lambda_E = 485$ nm due to pyrene–pyrene interactions. This band was also observed in the emission spectra of poly(DGEEA-co-PyBuAc) copolymers bearing 2% pyrene, but it was not perceived in the fluorescence spectrum of the sample bearing 1% of this chromophore. In contrast, in samples bearing 5 and 10% wt. pyrene content (Fig. 8b) a broader monomer emission band was seen at $\lambda_M = 402$ –423 nm followed by a broad excimer emission band centred at ca $\lambda_E = 495$ nm. This significant broadening and red shift of the emission bands reveal the presence of

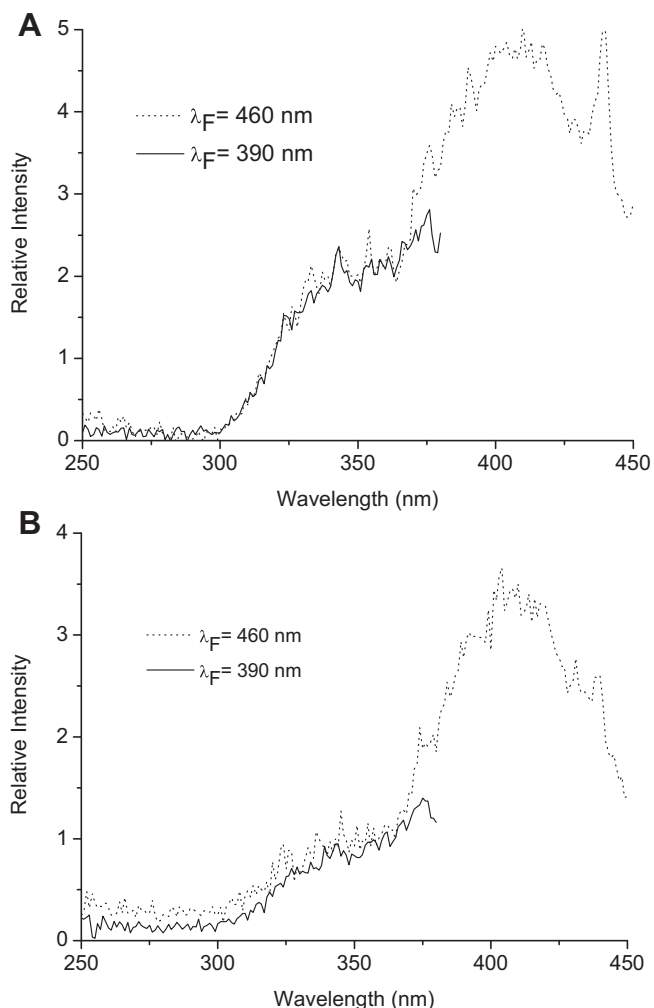


Fig. 9. Excitation spectra of poly(DGEEA-co-PyBuAc) copolymers: a) 5% wt. pyrene, b) 10% wt. pyrene.

pyrene–pyrene interactions and the predominance of pyrene in the associated form. Since the excimer emission band appears only in polymers with high pyrene content, these pyrene–pyrene interactions are mainly intermolecular. In order to explore the nature of the excimer emission, we recorded the excitation spectra of the poly(DGEEA-co-PyBuAc) copolymers. It is very well known that if



Fig. 10. Picture of the obtained luminescent materials.

the excitation spectrum recorded at λ_F of the “monomer emission” is equal to that at λ_F of the excimer emission, the excimer is dynamic in nature otherwise we have a static excimer [34].

The excitation spectra of poly(DGEEA-co-PyBuAc) copolymers bearing 5 and 10% wt. of pyrene are shown in Fig. 9a and b, respectively. As it can be observed, in both cases the excitation spectrum recorded at λ_F of the “monomer emission” and that recorded at λ_F of the excimer emission are almost the same. Therefore, both polymers give rise to the formation of dynamic excimers. In a previous work, we reported three model dimers in order to understand the influence of the geometry and internal stacking of the pyrene groups on their fluorescence spectra [40]. In the partially hydrogenated dimer DEPH, an excimer emission band was observed at $\lambda_E = 492$ nm, very close to that observed in the case of our polymers, which match well with the results obtained for the poly(DGEEA-co-PyBuAc) (5% and 10% wt.). In these polymers pyrene chromophores are linked to the flexible polymer backbone via an alkyl spacer, which allow them to move by diffusion to encounter each other.

These materials are blue-green emitters and the colour of the emitted light depends remarkably on the pyrene content (Fig. 10), giving rise to different tonalities: blue, caribbean blue or green. In the case of poly(DGEEA-co-PyBuAc)-1% wt. only monomer emission was observed whereas in poly(DGEEA-co-PyBuAc) (2, 5 and 10% wt. pyrene), both monomer and excimer emissions were detected in the blue and green regions, respectively.

Thus, FP showed to be a very efficient method to prepare very fast and easily luminescent polymers *in situ*. Jointly with the use of Trigonox-23 as initiator, this technique allows us to obtain homogeneous thick luminescent samples for practical applications. Contrarily to bulk polymerization together with the casting technique, FP permit us to prepare *in situ* luminescent polymer samples bearing diverse sizes and shapes and to elaborate light emitting devices with different thickness.

4. Conclusions

FP of DEGEEA was successfully achieved using Trigonox-23 as initiator with concentrations from 0.25 up to 10% wt. with respect to DEGEEA monomer. Unlike BPO, with this new initiator we were able to prepare homogeneous polymer samples without bubbling. DSC analysis showed that higher conversion values were obtained with this initiator. Moreover, the T_g values of the samples were almost equal and independent from Trigonox-23 concentration. On the other hand, light-emitting materials containing pyrene chromophores were obtained by frontal copolymerization DEGEEA with PyBuAc. A novel series of copolymers poly(DGEEA-co-PyBuA) bearing 1, 2, 5 and 10% wt. pyrene was obtained. UV–vis spectroscopy revealed that these polymers exhibit a maximum absorption band at $\lambda = 345$ nm. Fluorescence experiments of copolymers bearing pyrene contents higher than 2% wt. exhibited an intense excimer emission band due to the presence of intermolecular pyrene–pyrene interactions. Excitation spectra confirmed that these excimers are dynamic in nature. Finally, FP using Trigonox-23 as initiator showed to be a very promising method for the obtainment of thick luminescent polymer samples with a homogeneous morphology.

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