PEGDA-Based Luminescent Polymers Prepared by Frontal Polymerization

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ABSTRACT: Frontal polymerization (FP) of poly(ethylene glycol) diacrylate (PEGDA) was carried out using benzoyl peroxide (BPO) as radical initiator. In addition, a pyrene containing monomer, 1-pyrenebutyl acrylate (PyBuAc), was incorporated as a fluorescent probe in order to obtain luminescent materials with different chromophore contents. The resulting polymers were characterized by FT-IR spectroscopy in the solid state and their thermal properties were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Moreover, the optical properties of these materials were studied by absorption and fluorescence spectroscopy. The maximum amount of the incorporated pyrene-containing monomer into the polymer matrix was limited to 1 wt % by the polymerization process. The obtained labeled polymers poly(PEGDA-co-PyBuAc) exhibited a broad absorption band at 345 nm. The fluorescence spectra of these polymers exhibited mainly "monomer emission" so that no excimer emission was observed. It is possible to tune the color of the emitted light by varying the pyrene content in the samples. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 2890–2897

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INTRODUCTION Acrylic monomers bearing poly(ethylene glycol) (PEG) segments are useful building-block agents for the preparation of intelligent or bio-relevant materials, because nonend-capped poly(ethylene glycol) ether moieties make them amphiphilic or compatible with both polar and nonpolar solvents.[1] As a consequence, PEG derivatives are used as diluents and smoothing agents in the manufacture of paints, in the fabrication of nitrocellulose, baking finishes, as additives and for the combination of lacquers. Many PEG containing monomers are commercially available and can be polymerized either by anionic, radical, or living radical polymerization. One example is the poly(ethylene glycol) diacrylate (PEGDA) which is a monomer that has been primarily used in biomaterials science.[2,3]

Frontal polymerization (FP) is a process in which polymerization occurs in a directionally way through the reaction vessel, mostly using an external heating source to start a propagating front.[4] One of the most important factors to be considered in order to carry out a FP process is that the monomer does not have to spontaneously react at room temperature; however, the monomer must be very reactive upon ignition, thus quickly releasing a sufficient amount of polymerization heat to generate a self-sustaining propagating reaction front that converts monomer into polymer. This exothermicity allows the propagating front to self-sustain, since the amount of released heat during the reaction has to be larger than the heat lost in the reaction zone. Additionally, 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.[5] In general terms, FP is undoubtedly one of the most promising techniques because it offers many advantages over other traditional polymerization methods. For example: (1) because of the high temperatures reached by the fronts, FP generally guarantees reaction rates that are much larger than those found by using the classical polymerization techniques, (2) there is a low energy consumption because the external energy source is applied only for the brief time needed to ignite the polymerization reaction itself, whereas in a classical polymerization the energy source has to be maintained during the whole process, and (3) conversions are often larger than those obtained by the classical methods. In addition, no solvent is generally needed in the polymerization

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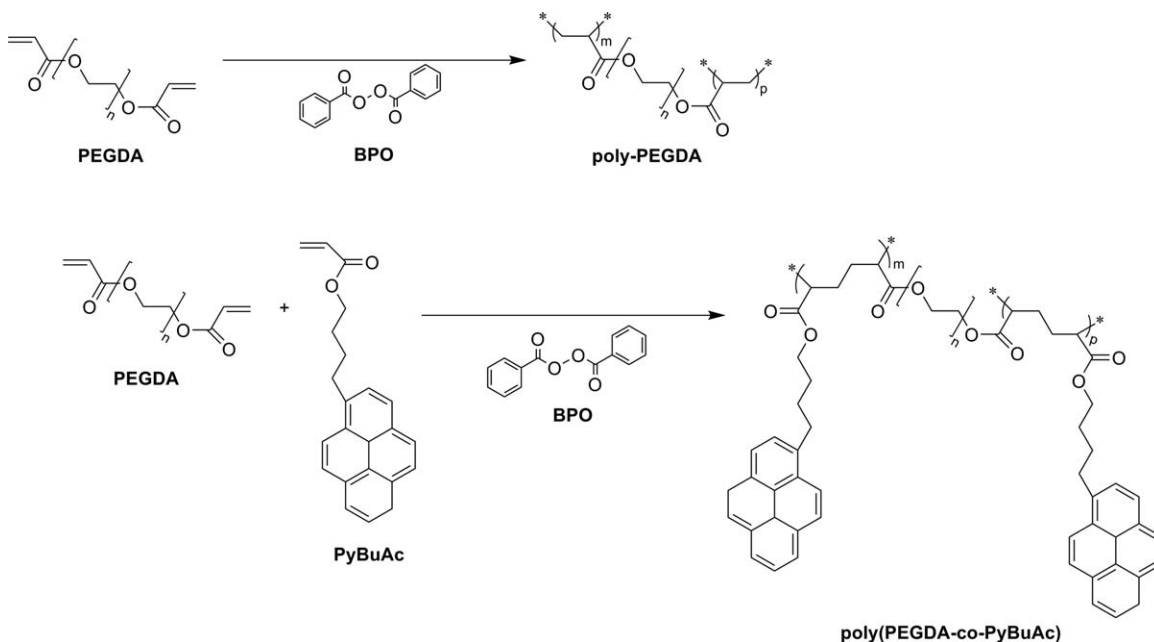
FIGURE 1 Synthesis of the obtained labeled polymers poly(PEGDA-co-PyBuAc).

mixture. Therefore, FP can be considered a very valuable approach in "green-chemistry."

FP was discovered in Russia in 1972 by Chechilo and Enikolopyan.[6] Since this early work, FP has attracted the attention of many groups that were involved in this research field. For example, Davtyan et al. studied the gel effect on the frontal radical polymerization of methyl methacrylate.[7] Later, Pojman carried out FP studies on acrylic monomers,[8,9] epoxy resins,[10,11] and urethane-acrylates.[12] They also investigated the formation of simultaneous-interpenetrating polymer networks,[13] the influence of the reactor geometry, the spin modes,[10] and the use of a microencapsulated initiator.[11,14] Scognamillo et al. employed FP to prepare hydrogels, polyacrylates, polyurethanes, nanocomposites, in the synthesis of stimuli-responsive materials, in the consolidation of porous materials, etc.;[15–25] Cai et al. achieved the FP of vinylpyrrolidone, 2-hydroxyethyl acrylate, and N-methylolacrylamide.[26–28] Finally, Davtyan et al. studied the frontal polymerization of vinyl monomers,[29,30] the frontal reaction of epoxy oligomers[31] and the incorporation of nanoparticles in the frontal copolymerization process.[32] In our research group we reported the copolymerization of three different polymer matrices with different chromophores in order to study NLO properties. Namely, PEGDA was copolymerized with the azochromophore (E)−2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl methacrylate (MDR-1);[33] 2-2-phenoxyethoxyacrylate (2-PEA) was also copolymerized with MDR-1 using two ionic liquids as initiators: tetrabutylphosphonium persulfate (TBPPS) and trihexyltetradecylphosphonium persulfate (TETDPPS).[34,35] Recently, bisphenol A ethoxylate diacrylate (BPAEDA) was copolymerized with two azobenzene-containing comonomers: MDR-1 and (E)−2-(4-((4-nitrophenyl)diazenyl)phenyl)−5,8,11-trioxa-2-azatridecan-13-yl methacrylate (4PEGMAN), using the ionic liq-

uid TETDPPS as radical initiator.[36] Particularly, PEGDA has attracted the interest of some researchers because it 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.[37,38]

Finally, pyrene has been considered as an efficient fluorescent probe and has been successfully used as a molecular label in the study of a large variety of polymers.[39–43] 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 scope of some reviews.[43,44] In the last 10 years our research group has incorporated pyrene into different polymers and well defined oligomers, in order to study the influence of the geometry of the molecule, the internal stacking and the pyrene-pyrene distance on the optical and photophysical properties of these compounds.[45–49]

Herein, we report the FP of PEGDA using benzoyl peroxide (BPO) as a radical initiator. The structure of the obtained polymers is shown in Figure 1. We investigated the influence of initiator concentration on the front velocity (V_f), maximum temperature (T_{max}), conversion degree, and temperature profiles. After having determined the optimal conditions for the FP of PEGDA, we performed the copolymerization of this monomer in the presence of 1-pyrenebutyl acrylate (PyBuAc), as co-monomer, in order to obtain light emitting polymers. These materials were characterized by FT-IR spectroscopy, and their thermal properties were evaluated by Thermogravimetric Analysis (TGA) and Differential Scanning
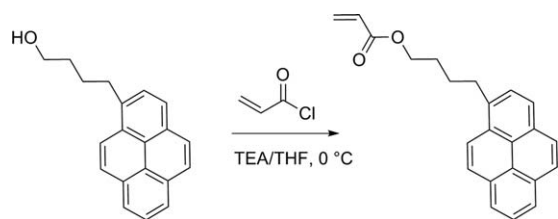
FIGURE 2 Synthesis of co-monomer PyBuAc.

Calorimetry (DSC). Finally, their optical properties were studied by absorption and fluorescence spectroscopy in the solid state.

EXPERIMENTAL

Materials

Poly(ethylene glycol) diacrylate (PEGDA, $M_n = 575$, $d = 1.12$ g mL^{-1}), triethylamine (TEA, formula weight (FW = 101.19, bp = 88.8 °C, $d = 0.726$ g·mL^{-1}), 1-pyrenebutanol (PyBuOH, FW = 274.36, mp = 80–83 °C), tetrahydrofuran (THF, FW = 72.11, bp = 65–67 °C, $d = 0.889$ g·mL^{-1}), benzoyl peroxide (BPO, FW = 242.23, mp = 102–105 °C) and acryloyl chloride (AcC, FW = 90.51, bp = 72–76 °C, $d = 1.114$ g·mL^{-1}) were purchased from Sigma-Aldrich. All reagents were used as received, without further purification.

Synthesis of 1-Pyrenebutyl Acrylate

The synthesis of 1-pyrenebutyl acrylate (PyBuAc) has been previously reported by us in the literature.[50,51] In this case, PyBuOH (2.000 g, 7.289 mmol) was dissolved in freshly distilled THF (50 mL) under argon atmosphere; then TEA (1.500 mL, 10.600 mmol) was added with a syringe to the solution. The mixture was cooled in an ice bath and AcC (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 column chromatography on silica gel, using a mixture hexanes:chloroform = 50:50 as eluent. PyBuAc was obtained as a yellow pale solid (Fig. 2).

Frontal Polymerization Experiments

In a glass test tube (16 cm length, 16 mm inner diameter), PEGDA (10 mL, 19.500 mmol) monomer and the appropriate amount of initiator (BPO, Table 1) were mixed together at room temperature until all the initiator was completely dissolved. Different PyBuAc concentrations were used, from 0.01 up to 1 wt % with respect to that of PEGDA. 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 amount of released heat 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 was calculated by measuring the distance recorded by the front in a given time and was expressed in cm min^{-1}.

Temperature profiles were determined using a K-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 glass walls of the tube, was measured as a function of the time. The synthesized polymers were removed from the test tubes and analyzed by DSC in order to determine their conversion degree and glass transition temperature (T_g). All samples were powdered and purified by soxhlet extraction with methanol in order to remove traces of remaining PyBuAc.

Characterization of the Obtained Polymers and the Labeled Monomer

Firstly, the FT-IR spectra of the monomers and the corresponding polymers were recorded on a Spectrum 100 (Perkin Elmer PRECISELY) spectrometer in KBr pressed pellets for the labeled monomer and the formed polymers. Polymerization of the samples was confirmed by comparing the FT-IR spectra of the polymers with those of the monomers. ^{1}H- and ^{13}C-NMR spectra of the labeled monomer in CDCl$_3$ solution were recorded at room temperature on a Bruker Advance 400 MHz spectrometer, operating at 400 MHz and 100 MHz for ^{1}H- and ^{13}C-, respectively. The thermal properties of the obtained polymers were studied by determining the glass transition temperature. DSC measurements were conducted in a DSC 2910 TA Instrument. For each sample, two consecutive scans were carried out from −80 to 250 °C with a heating rate of 5 °C min^{-1}, under N$_2$ atmosphere. Monomer conversion and T_g values were determined from

TABLE 1 PyBuAc Composition for the Prepared Copolymers

Sample	PyBuAc (wt %)	BPO (wt %)	V_f (cm·min^{-1})	T_{max} (°C)
Poly(PEGDA)	0	1	1.32	161
Poly(PEGDA-co-PyBuAc-0.01)	0.010	1	1.33	167
Poly(PEGDA-co-PyBuAc-0.025)	0.025	1	1.40	168
Poly(PEGDA-co-PyBuAc-0.05)	0.050	1	1.34	165
Poly(PEGDA-co-PyBuAc-0.1)	0.10	1	1.42	170
Poly(PEGDA-co-PyBuAc-0.25)	0.25	1	1.42	172
Poly(PEGDA-co-PyBuAc-0.5)	0.50	1	1.36	171
Poly(PEGDA-co-PyBuAc-1)	1.00	1	1.15	169

the first thermal scan. In all cases, the conversion was almost quantitative and was calculated by the following equation:

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

where ΔH_r (residual) is the peak area obtained from 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.

Absorption and fluorescence spectra of the pyrene-labeled monomer (PyBuAc) were recorded in THF (spectrophotometric grade), which was purchased from Sigma-Aldrich. Before 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 THF solution for PyBuAc (concentration 10^{-5} M), using a 1 cm quartz cell. It has been verified that the Lambert-Beer law applies for such concentration. The films were prepared by spin coating using a saturated solution of the polymers in chloroform. The thickness of the films were measured and resulted to be about 3 μm. 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). A solution of PyBuAc (concentration 10^{-6} M) was excited at the maximum absorption wavelength $\lambda = 345$ nm. For labeled polymers, emission spectra were recorded in film exciting at the same wavelength.

RESULTS AND DISCUSSION

Frontal Polymerization of PEGDA
Thermal frontal polymerization of PEGDA was carried out in a test tube, using the tip of a soldering iron as heating source. Table 1 shows the data of the front velocity and maximum temperature reached by the front as a function of PyBuAc co-monomer concentration for the FP process.

According to these results, we can observe that the front velocity decreases as the PyBuAc content increases from 0 to 1 wt %, which can be attributed to the lower reactivity of the labeled monomer with respect to that of PEGDA and to its larger molecular weight-to vinyl group ratio. When the PyBuAc concentration reaches the highest value, about 1 wt % respect to that of PEGDA, it should be noticed that, at this composition, the V_f shows its lowest value. Indeed, when larger amounts of PyBuAc were added, the propagating front was not able to self-sustain, thus resulting in stopping the polymerization process. This trend has been confirmed by plotting the front velocity vs the PyBuAc concentration (Fig. 3). In addition, it is worth to point out that the BPO radical initiator concentration was always kept constant at 1 wt % respect to the total amount of monomers. Meanwhile, the maximum temperature reached by the propagating front was in the range between 161 and 172 °C, so that this parameter
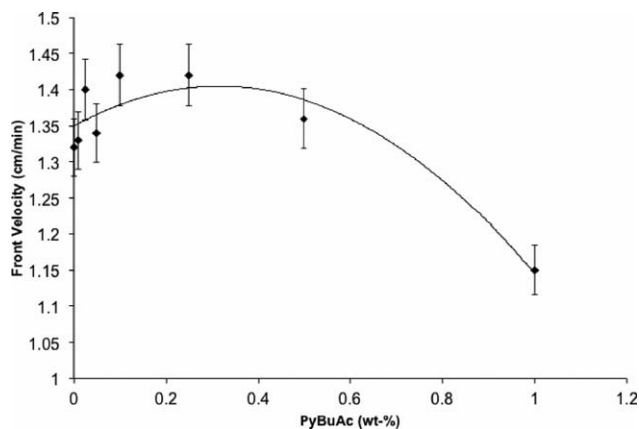

FIGURE 3 Front velocity versus PyBuAc concentration in the frontal polymerization of PEGDA.

is not significantly affected by the PyBuAc concentration. All polymers were obtained with very good conversion values, ranging from 94 to 98%.

Characterization of the Obtained Labeled Polymers
FT-IR spectra of PEGDA and poly(PEGDA) were recorded and the bands correspond to those previously reported by us.[50] In the FT-IR spectra of the different labeled polymers poly (PEGDA-co-PyBuAc) (not shown) we can observe a series of bands at 2980, 2870 (CH₂), 1720 (C=O), 1635 (C=C), 1290 (C—O ester), 1190, 1107, 1059 (C—O ethers) and 857, 710 (=C—H, out of plane) cm^{-1}. Particularly, the intense out of plane bands at 857 and 710 cm^{-1} (=C—H aromatic) clearly indicate that the PyBuAc co-monomer was successfully incorporated into the polymer backbone.

Thermal Properties of the Obtained Labeled Polymers
The thermal properties of the obtained polymers were determined by TGA and DSC (not shown). Nonlabeled poly (PEGDA) showed a T_{10} (10% weight loss temperature) value of 363 °C, exhibiting drastical degradation between 400 and 500 °C. However, the poly(PEGDA-co-PyBuAc) polymers showed similar T_{10} values about 370 °C since the amount of incorporated labeled monomer was quite low in all cases.

On the other hand, the glass transition temperature of the polymers was determined by DSC. Poly(PEGDA) showed a T_g value of −24 °C whereas the labeled polymers showed T_g values from −21 to −22 °C. From these results we can conclude that the incorporation of PyBuAc did not modify significantly the thermal properties of the obtained polymers since they show T_{10} and T_g values close to those of the nonlabeled poly(PEGDA).

Optical Properties of the Poly(PEGDA-co-PyBuAc) Polymers
The optical properties of the obtained polymers were studied by absorption and fluorescence spectroscopy in the solid state; the results are summarized in Table 2. The absorption spectra of the labeled monomer and the labeled polymers are shown in Figure 4. As we can see, polymers bearing high

TABLE 2 Optical Properties of the Labeled Polymers

| Sample	λ_{abs} (nm)	Cutoff (nm)	I_p/I_v	λ_{em} (nm)	Cutoff (nm)	Relative Quantum Yield (Φ)
Poly(PEGDA)	ND	375	ND	376, 396, 418	465	ND
Poly(PEGDA-co-PyBuAc-0.01)	ND	375	ND	376, 396, 418	465	0.40
Poly(PEGDA-co-PyBuAc-0.025)	ND	375	ND	376, 396, 418	465	ND
Poly(PEGDA-co-PyBuAc-0.05)	ND	375	ND	376, 396, 418	465	0.51
Poly(PEGDA-co-PyBuAc-0.1)	ND	375	ND	376, 396, 418	465	ND
Poly(PEGDA-co-PyBuAc-0.25)	345, 376	400	1.43	376, 396, 418	465	ND
Poly(PEGDA-co-PyBuAc-0.5)	345, 376	400	1.41	376, 396, 418	465	0.43
Poly(PEGDA-co-PyBuAc-1)	345, 376	400	1.4	376, 396, 418, 446	511	ND

ND = not determined.

pyrene content (poly(PEGDA-co-PyBuAc-1) and poly(PEGDA-co-PyBuAc-0.05)) show a well-structured absorption band at $\lambda = 345$ nm, due to the $S_0 \rightarrow S_2$ transition of the pyrene unit. This band can be also perceived in the absorption spectrum of the labeled monomer PyBuAc. Moreover, at $\lambda = 376$ nm we can observe a very low intensity band due to $S_0 \rightarrow S_1$ transition of pyrene, which can be seen only in concentrated solutions or in the solid state. However, in polymers bearing low pyrene content these absorption bands are not very visible and appear as an absorption tail.

According to Miyazawa and Winnik, from the absorption spectrum we can predict if there is preassociation of the pyrene units in the ground state.[44] Taking into account the absorption band at 345 nm, if the ratio $I_p/I_v < 3$ (where I_p is the intensity of the peak and I_v is the intensity of the valley) there is pyrene preassociation. However this parameter is more trustable for measurements in solution than in solid state.[44] Poly(PEGDA-co-PyBuAc-1) and poly(PEGDA-co-PyBuAc-0.25) showed a I_p/I_v value of 1.4, so we can affirm that some pyrene units are pre-associated. Pyrene-pyrene interactions can be detected by the ratio I_p/I_v of the absorption band appearing at 345 nm. The extent of pre-association can be quantified in solution in function of the pyrene concentration. In solid state we cannot quantify the percentage of pyrene-pyrene pre-association by means of this ratio.

For poly(PEGDA-co-PyBuAc-0.025) and poly(PEGDA-co-PyBuAc-0.01) we could not calculate this ratio because of the low pyrene content. However, in these samples we can assume that there is no pre-association of the pyrene chromophores, which was further confirmed by fluorescence spectroscopy.

The fluorescence spectra of the obtained polymers were recorded in solid state by exciting at $\lambda = 345$ nm (Fig. 5). As we can see, all the emission spectra of the obtained polymers are very similar in shape and show different intensities depending on the pyrene content. For instance, the fluorescence spectrum of low pyrene content polymer poly(PEGDA-co-PyBuAc-0.01) [Fig. 5(a)] exhibits a well-structured emis-

sion band at $\lambda_M = 376$–418 nm due to the "monomer emission" of pyrene in the no-associated state. In this polymer, no excimer emission is observed, which reveals the absence of pyrene association or pyrene-pyrene interactions.
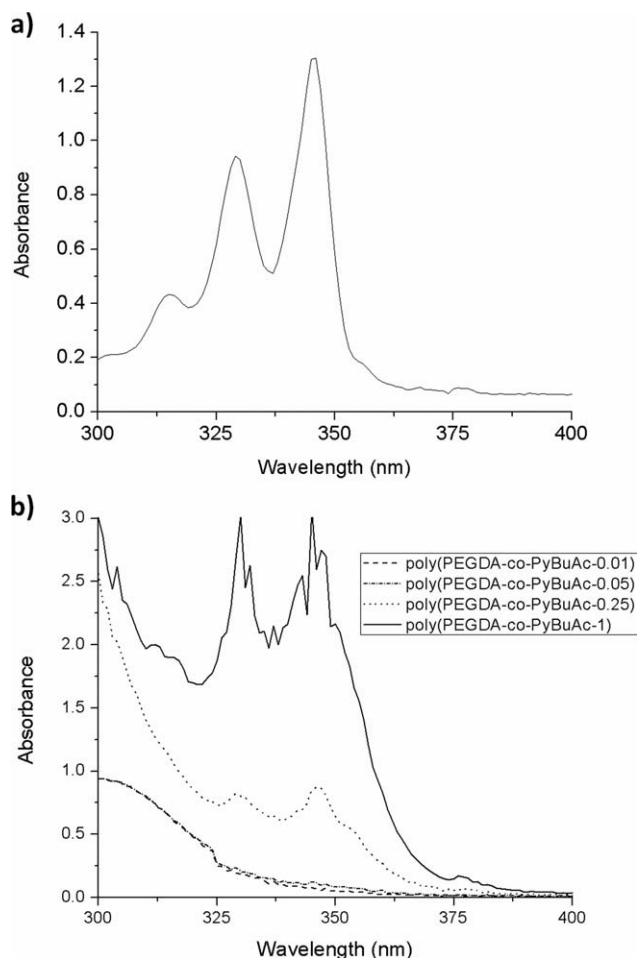
FIGURE 4 Absorption spectra of (a) PyBuAc and (b) poly(PEGDA-co-PyBuAc) polymers.

Polymers poly(PEGDA-*co*-PyBuAc-0.05) and poly(PEGDA-*co*-PyBuAc-0.25) behaved similarly and did not show any excimer emission. However, when we recorded the fluorescence spectra of the sample containing the highest pyrene content poly(PEGDA-*co*-PyBuAc-1), this polymer showed a broadening of the monomer emission band, which appears at $\lambda_M = 376$–418 nm, followed by a discrete emission tail beyond 450 nm. Although apparently there is no excimer emission, the occurrence of traces of pyrene-pyrene preassociation can also be detected in some samples by the presence of a slight emission beyond 450 nm (see Fig. 5), a wavelength where pyrene itself does not emit. The emission cut off of this polymer appears at 511 nm (65 nm redshifted with respect to those of the other polymers). These features reveal the presence of some pyrene-pyrene interactions in this polymer. These polymers are blue emitters and exhibit mainly "monomer emission," which can be due to the fact that the cross-linked structure of the polymer matrix restrains the mobility of the pyrene units thereby preventing their interaction to form excimers. Very intense excimer emission bands have been observed in other labeled polymers previously reported by us.[50,51]

In a previous work, we carried out the thermal frontal polymerization (FP) of di(ethylene glycol) ethyl ether acrylate (DEGEEA) in the presence of the same labeled monomer PyBuAc.[50] Unlike PEGDA, this monomer allowed the incorporation up to 10 wt % of the labeled monomer because it was very soluble in DGEEA. The obtained poly(DGEEA-*co*-PyBuAc) polymers showed the presence of pyrene-pyrene interactions that was detected by the presence of excimers. However, the polymers obtained with PEGDA are more resistant and thermally more stable because of their cross-linked structure. The most important feature of this approach is that we can tune the colour emission of the obtained material by varying the pyrene content, since pyrene shows a blue emission in the no-associated state
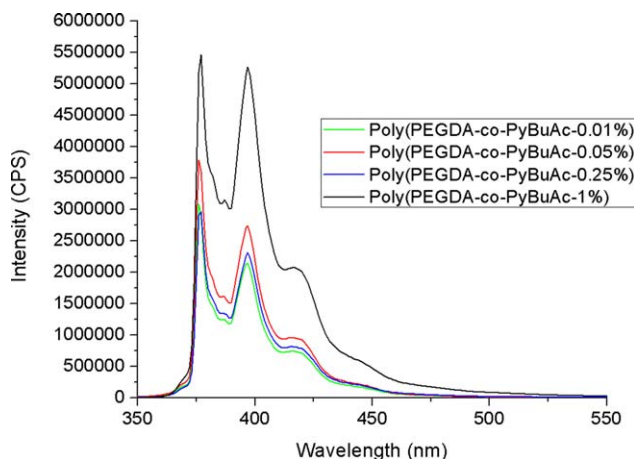

FIGURE 6 Images of the obtainment of poly(PEGDA-*co*-PyBuAc) polymers during the frontal polymerization reaction. (a) Normal and (b) exposed to UV light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(low concentration) and caribbean blue emission in the associated state (high concentration) (Fig. 6).

CONCLUSIONS

The synthesis of a new series of PEGDA based polymers containing pyrene groups, poly(PEGDA-*co*-PyBuAc), was successfully achieved by frontal polymerization (FP) using benzoyl peroxide (BPO) as initiator. The obtained polymers showed a good thermal stability with T_{10} values of about 370 °C, very close to that of the polymer matrix. It is evident that the incorporation of the pyrene chromophores did not modify significantly the thermal properties of the obtained polymers. The obtained labeled polymers poly(PEGDA-*co*-PyBuAc) exhibited a broad absorption band at 345 nm due

FIGURE 5 Emission spectra of the poly(PEGDA-*co*-PyBuAc) polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
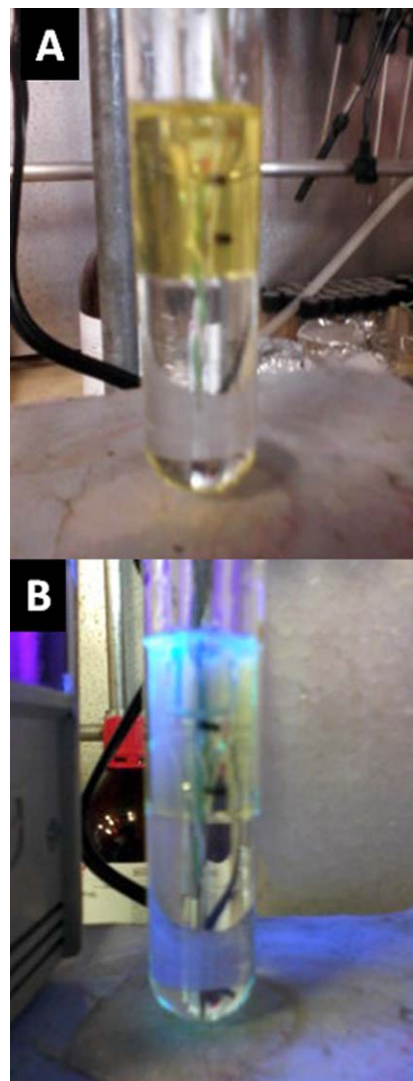
to the $S_0 \rightarrow S_2$ transition of the pyrene moieties and a second discrete band at 376 nm due to the $S_0 \rightarrow S_1$ transition of the same chromophore. Unlike other pyrene-containing polymers obtained by frontal polymerization, the fluorescence spectra of these polymers exhibited mainly "monomer emission" at 376 to 418 nm so that no excimer emission was observed. It is possible to tune the color of the emitted light by varying the pyrene content in the samples.

ACKNOWLEDGMENTS

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