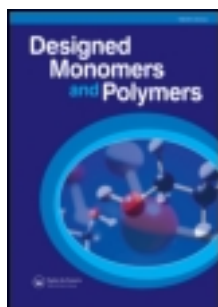


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Synthesis and characterization of novel polymers bearing fluorescein units: thermal and optical properties

Jair A. Esquivel-Guzmán, Gerardo Zaragoza-Galán, Jesús Ortíz-Palacios and Ernesto Rivera*

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In this work, we report the synthesis and characterization of four novel series of copolymers bearing fluorescein moieties. Two monomers: fluorescein methacrylate and dimethacrylate were prepared and were copolymerized in the presence of four different acrylic monomers bearing oligo(ethylene glycol) segments: ethylene glycol phenyl ether acrylate, ethylene glycol phenyl ether methacrylate, poly(ethylene glycol) methyl ether acrylate ($M_n=475$ g/mol), and poly(ethylene glycol) methyl ether methacrylate ($M_n=480$ g/mol). The obtained copolymers were fully characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy. Their thermal properties were determined by thermogravimetric analysis and differential scanning calorimetry, and their optical properties were studied by absorption and fluorescence spectroscopy in solution and in solid state.

Keywords: polymer; fluorescein; poly(ethylene glycol); optical properties

Introduction

In the last years, there has been an increasing demand of luminescent materials for practical uses so that research on fluorescent polymers has been considered a subject of interest for the scientific community [1]. These compounds have a wide range of important applications, for example, they are used as luminescent coatings, fluorescent probes, fluorescent sensors, solid-state dye lasers, and for the preparation of materials for luminescence conversion (LUCO) [2–17]. A technique which has been normally used to introduce fluorescent dyes into a polymer matrix is dissolving the dye into a monomer to promote a further *in situ* polymerization. In this case, the obtained material is a physical dispersion of the dye in the polymer matrix. A disadvantage of this method is that not all the chromophores show a good solubility in the monomers where they have to be dispersed prior to polymerization, which leads to the formation of dye aggregates in the polymer matrix or provoke phase separation, thereby producing materials with poor optical properties. Another procedure to obtain more efficient fluorescent materials is the synthesis of a label monomer containing a fluorescent group, which can be further copolymerized with a wide variety of monomers [10,13,18–21]. Moreover, this chromophore is commercially available and can be functionalized giving rise to a wide variety of derivatives which can be employed for several technical applications [23].

Many efforts on designing polymers bearing fluorescein units in their structure have been extensively done. Uthirakumar et al. [18] synthesized a series of polyesters with fluorescein

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units in their backbone by copolymerization of poly(fluoresceinyl terephthalate) with bisphenol-A terephthalate. The obtained polymers showed low molecular weights, high solubility, and a good thermal stability, as well as promising emission of white light from a blue source, which make them good prospects for the development of LUCO materials [19].

An interesting method to prepare polymers containing fluorescein was developed by Silcoff and coworkers. They synthesized a series of fluorescein compounds containing saturated chains linked to terminal resorcinol units, based on the classic synthesis of fluorescein developed by von Baeyer in 1871. These compounds were reacted with phthalic anhydride in the presence of methanesulfonic acid to give the corresponding fluorescein containing polymers [20]. These materials showed very similar optical properties to those of fluorescein, exhibiting a better photochemical stability than the chromophore itself.

Another attempt to prepare fluorescein containing polymers with well-defined structures was reported by Li et al. [21] who synthesized two bromine-containing monomers derived from fluorescein, which were further polymerized by atom transfer radical polymerization in the presence of methyl methacrylate to give a series of polymers having fluorescein units in the backbone with good molecular weights and narrow polydispersity values. Recently many promising fluorescent polymers bearing different structures [18–21,23,24–38], some of them containing fluorescein, have been reported in the literature [15,17,18–21,23,24–26]. However, we are interested in the development of fluorescent polymers exhibiting an amphiphilic behavior or at least able to swell in the presence of water [31]. For that, we incorporated oligo(ethylene glycol) segments into our polymer systems in order to confer them water compatibility.

In the present work, we report the development of a novel series of polymers bearing fluorescein units prepared by solution copolymerization of fluorescein methacrylate (**Flu-MA**) and fluorescein dimethacrylate (**Flu-DMA**) with four commercial acrylic monomers. Polymerizations were performed using azo-bis-isobutyronitrile (AIBN) as initiator and anhydrous tetrahydrofuran (THF) as solvent. The thermal properties of the obtained copolymers were determined and compared with those of their corresponding homopolymers. Moreover, their optical properties were studied by absorption and fluorescence spectroscopy with respect to those of the employed fluorescein monomers.

Experimental part

All reagents were purchased from Aldrich Chemical Co. and used as received. THF was dried by reflux with sodium, using benzophenone as indicator. Prior to use, chloroform was dried by stirring in the presence of CaH₂. Solvents employed for flash column chromatography were purchased from Tecsiquim.

FTIR spectra of the compounds were obtained with a Nicolet 6700 spectrometer bearing a Smart Orbit ATR detector, in KBr pressed pellet for solids and film for liquids. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 instrument operating at 400 and 100 MHz for ¹H and ¹³C NMR, respectively. Absorption spectra were measured on a UNICAM UV-300 spectrophotometer in THF solution for monomers and in thin films for the polymers. Fluorescence spectra were recorded at room temperature in a Cary Eclipse UV-Varian fluorometer, exciting at the maximum absorption wavelength of fluorescein ($\lambda = 460$ nm).

Thermogravimetric analysis (TGA) of the polymers was carried out in a Hi-Res TGA 2950 Instrument, from 0 to 600 °C under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were recorded on a Jeol JSM-70 instrument, containing a Leica Quantiment 500 image analyzer equipment, from –50 to 250 °C with a heating rate of 10 °C/min.

Synthesis of the monomers

Fluorescein methacrylate

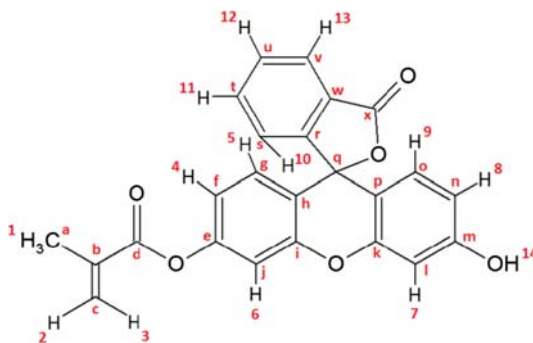
In a round-bottom three-neck flask, fluorescein (0.332 g, 1 mmol) was dissolved in 100 mL of dry THF at 25 °C with stirring under inert atmosphere. Then triethylamine (0.108 g, 1.07 mmol) was added. Methacryloyl chloride (0.108 g, 1.03 mmol) dissolved in THF (5 mL) was added dropwise to the fluorescein solution. The reaction mixture was kept under an ice bath with stirring for 1 h and then at room temperature for 24 h. Furthermore, THF was evaporated and the crude product was purified by column chromatography using CHCl₃: acetone 97: 3 as eluent. The pure product was obtained as a yellow powder. Yield: 73%.

FTIR (ATR) (KBr): 3391 (s; OH), 3070 (s; CH), 1764 (s; C=O), 1736 (s; C=O), 1612, 1464, 1426 (s; aromatic ring), 1247, 1115 (s; C–O) and 1165 (s; C–O) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) (Scheme 1): δ=8.05–8.04 (d, *J*=7.3, 1H), 7.66–7.64 (m, 2H), 7.15–7.13 (d, *J*=9.5, 2H), 6.83 (s, 2H), 6.73–6.72 (m, 1H), 6.67–6.65 (d, *J*=8.6, 1H), 6.57–6.54 (dd, *J*=8.6, 2.1, 1H), 6.39 (s, 1H), 5.82 (s, 1H), 2.09 (s, 3H) ppm. ¹³C NMR (DMSO-d₆, 400 MHz) (Scheme 1) δ=169.13 (1C, C^x), 165.42 (1C, C^d), 160.13 (1C, C^m), 152.73 (1C, C^r), 152.41 (1C, C^c), 152.01 (1C, C^k), 151.64 (1C, C^l), 136.34 (1C, C^l), 135.40 (1C, C^b), 130.84 (1C, C^o), 129.55 (1C, C^s), 129.46 (1C, C^u), 128.81 (1C, C^c), 126.19 (1C, C^w), 125.32 (1C, C^v), 124.44 (1C, C^g), 118.57 (1C, C^h), 117.07 (1C, C^f), 113.59 (1C, Cⁿ), 110.86 (1C, C^j), 109.57 (1C, C^p), 102.78 (1C, C^l), 82.53 (1C, C^q), 18.41 (1C, C^a) ppm.

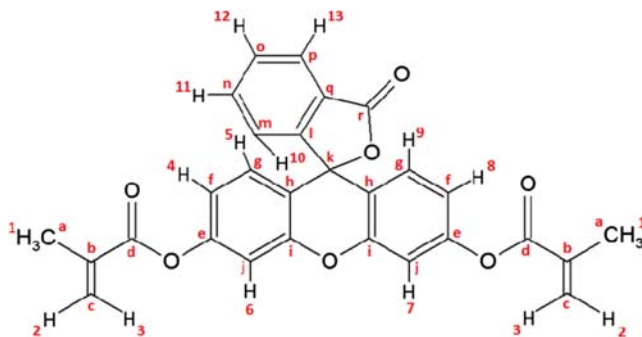
Fluorescein dimethacrylate

In a round-bottom three-neck flask, fluorescein (0.332 g, 1 mmol) was dissolved in THF (100 mL) under inert atmosphere. The resulting solution was cooled to 0 °C with an ice bath; then triethylamine (0.362 g, 3.58 mmol) was added. Afterward, methacryloyl chloride (0.269 g, 2.57 mmol) dissolved in THF (5 mL) was added dropwise to the fluorescein solution. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 19 h. After this time, a trace of hydroquinone was added to the solution in order to prevent an undesired polymerization; then THF was evaporated at reduced pressure. The obtained solid was purified by column chromatography using CHCl₃:acetone 99:1 as eluent. The pure product was obtained as transparent crystals. Yield: 70%.

FTIR (ATR) (KBr): 3075 (s; CH), 3022 (s; CH), 2962 (s; CH), 1770 (s; C=O), 1739 (s; C=O), 1613, 1493, 1421 (s; aromatic ring), 1240, 1120 (s; C–O) y 1156 (s; C–O) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) (Scheme 2) δ=8.07 (d, *J*=7.1, 1H), 7.71–7.66 (m, 6.5, 2H), 7.21 (t, *J*=8.1, 1H), 7.15 (s, 2H), 7.10 (s, 1H), 6.87 (s, 2H), 6.80 (m, 1H), 6.38 (s, 2H), 5.81 (s,



Scheme 1. Structure of Flu-MA.



Scheme 2. Structure of Flu-DMA.

2H), 2.08 (s, 6H) ppm. ^{13}C NMR (CDCl_3 , 400 MHz) (Scheme 2) δ = 169.14 (1C, C^r), 165.26 (2C, C^d), 152.97 (1C, C^l), 152.35 (2C, C^e), 151.62 (2C, C^i), 136.55 (1C, C^n), 135.31 (2C, C^b), 130.11 (1C, C^o), 130.06 (1C, C^m), 128.96 (2C, C^c), 126.12 (1C, C^q), 125.24 (1C, C^p), 124.11 (2C, C^g), 117.93 (2C, C^h), 116.39 (2C, C^f), 110.47 (1C, C^j), 81.13 (1C, C^k), 18.37 (1C, C^a) ppm.

Copolymerization of Flu-MA and Flu-DMA with acrylic monomers

Series of copolymers were obtained by copolymerizing both monomers **Flu-MA** and **Flu-DMA** with four commercially available acrylic monomers (ethylene glycol phenyl ether acrylate [**EGPEA**], ethylene glycol phenyl ether methacrylate [**EGPEM**], poly(ethylene glycol) methyl ether acrylate [**PEMEA**], and poly(ethylene glycol) methyl ether methacrylate [**PEMEM**], whose structures are shown in Table 1 (*vide infra*). A general diagram of copolymerization of **Flu-MA** and **Flu-DMA** with the different acrylic monomers is shown in Figure 1 (*vide infra*).

Synthesis of copolymers containing Flu-MA

Flu-MA (0.026 g, 0.064 mmol) was dissolved in THF (4 mL); then the appropriate amount of acrylic monomer (**EGPEM**, **EGPEA**, **PEMEM**, or **PEMEA**) was added (2.61 mmol). The copolymerizations were carried out at 60 °C under inert atmosphere in the darkness for 90 h [4]. The obtained copolymers were precipitated and purified by washing them with methanol, after dissolving them with chloroform. These steps were repeated until the methanol addition did not produce turbid solutions.

For **poly(EGPEA-co-Flu-MA)**: ^1H NMR (400 MHz) δ = 8.02 (1H), 7.58 (2H), 7.27 (36H), 6.90 (55H), 4.35 (35H), 4.05 (38H), 2.51 (19H), 1.71 (22H) ppm.

For **poly(EGPEM-co-Flu-MA)**: ^1H NMR (400 MHz) δ = 8.05 (1H), 7.63 (2H), 7.26 (38H), 6.90 (54H), 4.06 (72H), 1.85 (32H), 0.96 (37H) ppm.

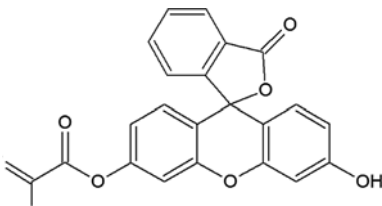
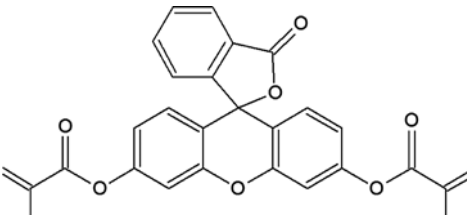
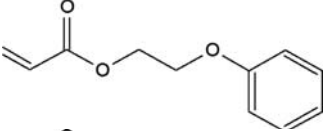
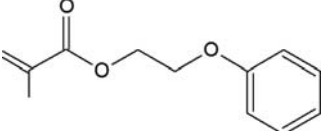
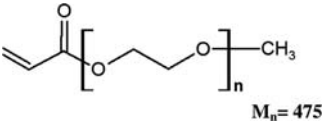
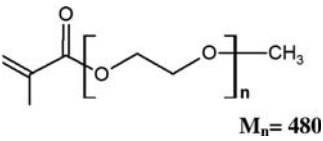
For **poly(PEMEA-co-Flu-MA)**: ^1H NMR (400 MHz) δ = 7.86 (1H), 3.41 (940 H), 3.14 (54 H), 2.74 (20 H), 2.14 (29 H) ppm.

For **poly(PEMEM-co-Flu-MA)**: ^1H NMR (400 MHz) δ = 7.92 (1H), 3.37 (30H), 3.09 (1H), 0.71 (3H) ppm.

Synthesis of copolymers containing Flu-DMA

Copolymers of **Flu-DMA** were prepared following a similar procedure. Different solutions of **Flu-DMA** (0.030 g, 0.064 mmol) in CHCl_3 (4 mL) were prepared; then the appropriate

Table 1. Monomers employed in the synthesis.

Monomer	Symbol	Structure
Fluorescein methacrylate	Flu-MA	
Fluorescein dimethacrylate	Flu-DMA	
Ethylene glycol phenyl ether acrylate	EGPEA	
Ethylene glycol phenyl ether methacrylate	EGPEM	
Poly(ethylene glycol) methyl ether acrylate	PEMEA	
Poly(ethylene glycol) methyl ether methacrylate	PEMEM	

amount of the respective acrylic monomer (2.61 mmol) and AIBN (0.02 g, 0.12 mmol) was added. The polymerizations were carried out at 60 °C, in the darkness under nitrogen atmosphere for 90 h.

For **poly(EGPEA-co-Flu-DMA)**: ^1H NMR (400 MHz) δ = 8.06 (1H), 7.64 (2H), 7.27 (33H), 6.90 (46H), 4.39 (30H), 4.05 (28H), 2.49 (16H), 1.70 (23H) ppm.

For poly(EGPEM-co-Flu-MA): (insoluble)

For **poly(PEMEA-co-Flu-DMA)**: ^1H NMR (400 MHz) δ = 7.99 (1H), 7.10 (2H), 6.75 (2H), 3.54 (272 H), 3.27 (34 H), 2.79 (6 H), 2.20 (12) ppm.

For **poly(PEMEM-co-Flu-DMA)**: ^1H NMR (400 MHz) δ = 8.00 (1H), 3.54 (63H), 3.27 (7H), 0.80 (5H) ppm.

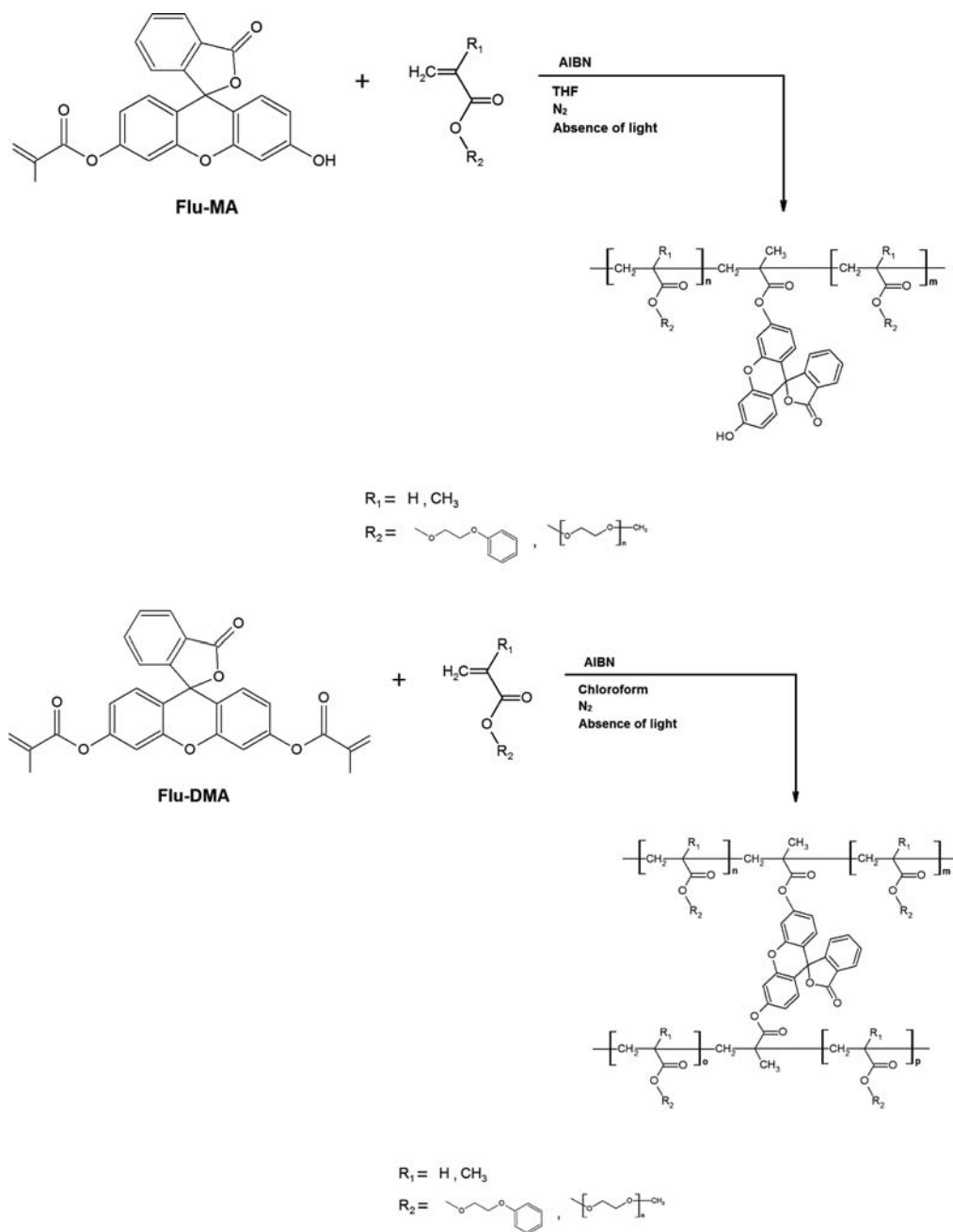


Figure 1. Synthesis of the copolymers.

Results and discussion

Synthesis and characterization of the polymers

Flu-MA and **Flu-DMA** were prepared by reacting 1 equivalent of fluorescein in the presence of 1 and 2 equivalents of methacryloyl chloride, respectively, using THF as solvent and tri-

ethylamine as catalyst. The fluorescein monomers were fully characterized by FTIR, ^1H , and ^{13}C NMR spectroscopies and the assignment of the signals is included in the experimental section. These compounds were copolymerized in the presence of four different acrylic monomers: **EGPEA**, **EGPEM**, **PEMEA** ($M_n=475$ g/mol), and **PEMEM** ($M_n=480$ g/mol). The copolymerization of **Flu-MA** and **Flu-DMA** with **EGPEA** ($R_1=\text{H}$, $R_2=\text{PhOCH}_2\text{CH}_2\text{O}$), **EGPEM** ($R_1=\text{CH}_3$, $R_2=\text{PhOCH}_2\text{CH}_2\text{O}$), **PEMEA** ($R_1=\text{H}$, $R_2=-(\text{OCH}_2\text{CH}_2)_n\text{CH}_3$), and **PEMEM** ($R_1=\text{CH}_3$, $R_2=-(\text{OCH}_2\text{CH}_2)_n\text{CH}_3$) is shown in Figure 1, respectively.

All copolymerizations were carried out by reacting 20% mol of **Flu-MA** or **Flu-DMA** with the appropriate amount of the acrylic or methacrylic monomer in THF solution using AIBN as initiator under inert atmosphere at 60°C . Most of the obtained copolymers showed to be partially soluble in some common organic solvents such as toluene, THF, and chloroform. Similarly the acrylic and methacrylic monomers **EGPEA**, **EGPEM**, **PEMEA**, and **PEMEM** were homopolymerized in order to obtain **poly(EGPEA)**, **poly(EGPEM)**, **poly(PEMEA)**, and **poly(PEMEM)**, which were used as references for comparison purposes. Since the insoluble part predominates, we determined only the molecular weights of the soluble part of the polymers, which resulted to be oligomers with low molecular weights.

Structural characterization of the obtained polymers and copolymers was carried out by FTIR in KBr pressed pellets and ^1H NMR spectroscopy in gel. A comparison between ^1H NMR spectrum of **poly(EGPEM)** and **poly(EGPEM-co-Flu-MA)** in gel is shown in Figure 2.

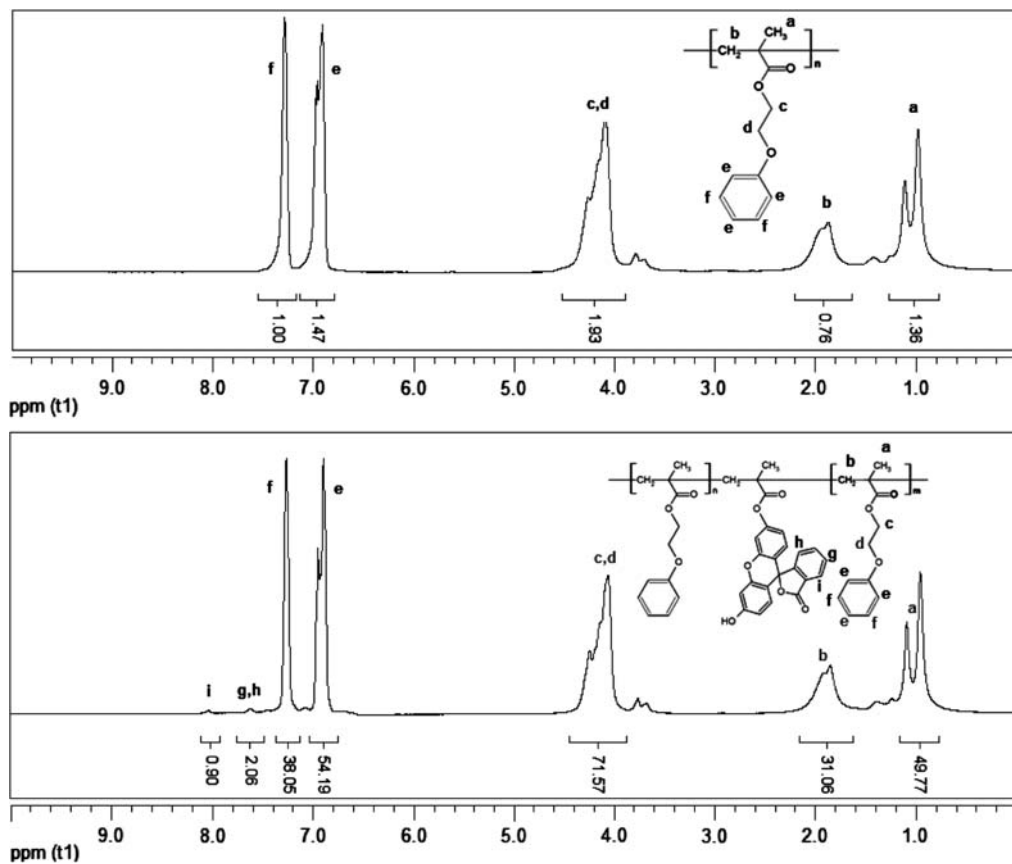


Figure 2. Comparison between **poly(EGPEM)** and **poly(EGPEM-co-Flu-MA)**.

In the ^1H NMR spectrum of **poly(EGPEM-co-Flu-MA)**, we can observe the signals due to the protons present in the fluorescein units at 8.02 (H_i) and 7.63 (H_g and H_h) ppm, which are not very intense because of the low content of the labeled units in the copolymer. It is worth to point out that apparition of these signals jointly with the lack of the signals of the vinyl protons of the **Flu-MA** clearly indicates a successful incorporation of the fluorescein chromophore, which is covalently bonded to the polymer backbone. In contrast, we can observe the intense polymer matrix signals at 7.26 (H_c), 6.90 (H_f), 4.06 (H_c , H_d), 1.85 (H_b), 0.96 (H_a) ppm.

The ^1H NMR spectra of the other copolymers showed a similar behavior, where the signals of the polymer matrix are more intense than those corresponding to the fluorescein units. However, in all cases the incorporation of **Flu-MA** or **Flu-DMA** was successful; the assignment of the signals of the other obtained copolymers has been included in the experimental section.

Thermal properties of the polymers

The thermal properties of the obtained polymers and copolymers were studied by TGA and DSC and the results are summarized in Table 2.

From TGA measurements, we can see that all polymers exhibited from middle to good thermal stabilities with T_{10} values between 361 and 138 °C. Since the fluorescein content in all polymers is very low, in some cases, the differences in thermal stability are negligible. For instance in the **poly(EGPEA)** series, we can notice that the homopolymer ($T_{10}=360$ °C) showed a good thermal stability very close to those of its copolymers **poly(EGPEA-co-Flu-MA)** ($T_{10}=352$ °C) and **poly(EGPEA-co-Flu-DMA)**. The latter is a cross-linked polymer showed higher T_{10} value than its homolog **poly(EGPEA-co-Flu-MA)**, very close to that **poly(EGPEA)**. These polymers exhibited a T_{10} around 350–360 °C and drastic degradation from 230 to 470 °C. Polymers of the **poly(EGPEM)** series behaved similarly with different changes in their T_{10} values.

Copolymers obtained with **PEMEA** and **PEMEM** monomers, which have oligo(ethylene glycol) segments gave polymers with a more flexible structure. Figure 3 shows the TGA curve for the **poly(PEMEA)** series. As we can see, **poly(PEMEA-co-Flu-MA)** ($T_{10}=328$)

Table 2. Thermal properties of the fluorescein containing polymers.

Polymer	T_{10} (°C) ^a	Critic degradation range (°C)	T_g (°C) ^a
Poly(EGPEA)	360	310–470	15
Poly(EGPEA-co-Flu-MA)	352	310–470	19
Poly(EGPEA-co-Flu-DMA)	361	330–470	18
Poly(EGPEM)	199	250–440	42
Poly(EGPEM-co-Flu-MA)	209	230–460	51
Poly(EGPEM-co-Flu-DMA)	ND ^b	ND ^b	ND ^b
Poly(PEMEA)	210	300–452	–
Poly(PEMEA-co-Flu-MA)	328	312–459	–
Poly(PEMEA-co-Flu-DMA)	166	314–464	–
Poly(PEMEM)	162	270–437	–
Poly(PEMEM-co-Flu-MA)	230	279–442	–
Poly(PEMEM-co-Flu-DMA)	138	298–444	–

^aHeating rate 10 °C/min.

^bNot determined, since the polymer could not be characterized because of its insolubility.

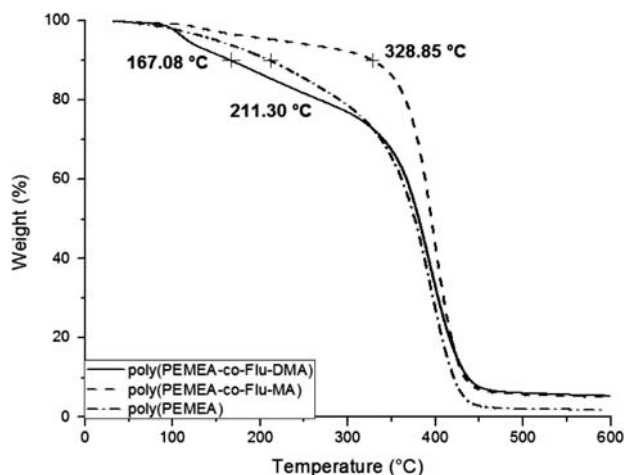


Figure 3. TGA of the obtained polymers of the **poly(PEMEA)** series.

showed higher thermal stability than that presented by **PEMEA** ($T_{10}=210$). Contrarily to what could be expected, **poly(PEMEA-co-Flu-DMA)**, which should have a cross-linked structure, exhibited a considerably lower thermal stability ($T_{10}=166$ °C) than **poly(PEMEA)**. As we can notice, the **poly(PEMEM)** showed exactly the same tendency with T_{10} values of 162, 230 and 138 °C for **poly(PEMEM)**, **poly(PEMEM-co-Flu-MA)**, and **poly(PEMEM-co-Flu-DMA)**, respectively.

It is very well known that poly(ethylene glycol) is very flexible and possesses a low thermal stability, that is why polymers belonging to the **poly(EGPEA)** and **poly(EGPEM)** series exhibited higher T_g values than those of the **poly(PEMEA)** and **poly(PEMEM)** derivatives. The fact that the cross-linked copolymers **poly(PEMEA-co-Flu-DMA)** and **poly(PEMEM-co-Flu-DMA)** exhibited lower T_{10} values than their corresponding homopolymers without fluorescein can be explained by the fact that degradation in acrylic polymers starts at unsaturated chain ends (weak links) which are formed during the termination step of radical polymerization. In principle, the onset of weight loss of cross-linked polymers is usually lower than that of linear polymers. However, it is possible that the radical copolymerization of bifunctional acrylic monomers instead of giving totally cross-linked polymers resulted in the obtaining of partially cross-linked polymers bearing a high content of unreacted double bonds [26]. Glass transition temperatures (T_g) of the copolymers of the **poly(EGPEA)** and **poly(EGPEM)** series were determined by DSC and the values are summarized in Table 2. Their copolymers bearing **Flu-MA** and **Flu-DMA** units showed higher T_g values than those presented by their respective homopolymers, since the aromatic fluorescein units and cross-linking, in the case of copolymers prepared with **Flu-DMA**, confer higher rigidity to their structure thereby restraining the mobility of the chains.

Optical properties of the monomers and the copolymers

Optical properties of copolymers bearing fluorescein units were studied by absorption spectroscopy in the UV–vis range and the results were compared to those obtained with their corresponding homopolymers containing dispersed fluorescein; the experiments were carried out in thin film. Figure 4 shows the absorption spectra of fluorescein, **Flu-MA** and **Flu-DMA** monomers in methanol. As we can see, fluorescein exhibits two absorption bands at

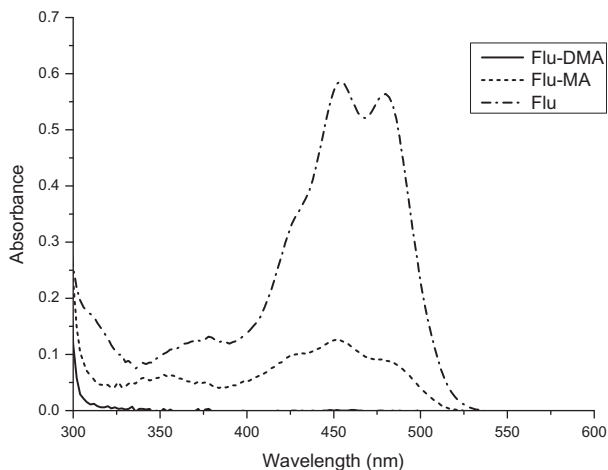


Figure 4. Absorption spectra of fluorescein and the monomers **Flu-MA** and **Flu-DMA**.

$\lambda = 278$ nm ($\pi-\pi^*$) and $\lambda_{\max} = 468$ nm ($n-\pi^*$) due to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively. Similarly, monomer **Flu-MA** shows the same bands, which appear at $\lambda = 276$ nm ($\pi-\pi^*$), and $\lambda = 452$ nm ($n-\pi^*$).

Apparently, monomer **Flu-DMA** shows only one absorption band at $\lambda = 288$ nm ($\pi-\pi^*$) due to the $S_0 \rightarrow S_2$; here the $n-\pi^*$ cannot be observed. This can be due to the fact that the $n-\pi^*$ transition is highly influenced by the heteroatoms present in the fluorescein units so that the esterification of the hydroxyl groups diminishes notably the molar extinction coefficient of this compound thereby, decreasing intensity of its absorption bands.

According to the literature [39], fluorescein shows an emission band in ethanol solution at $\lambda_F = 500$ nm upon excitation at $\lambda_{\text{exc}} = 470$ nm. The fluorescence spectra of fluorescein and the above mentioned monomers in methanol solution obtained at $\lambda_{\text{exc}} = 450$ nm are shown in Figure 5. As we can notice, fluorescein in methanol solution shows an emission band at $\lambda_F = 515$ nm followed by a discrete shoulder at 541 nm, which is due to the $S_1 \rightarrow S_0$ transition for this chromophore.

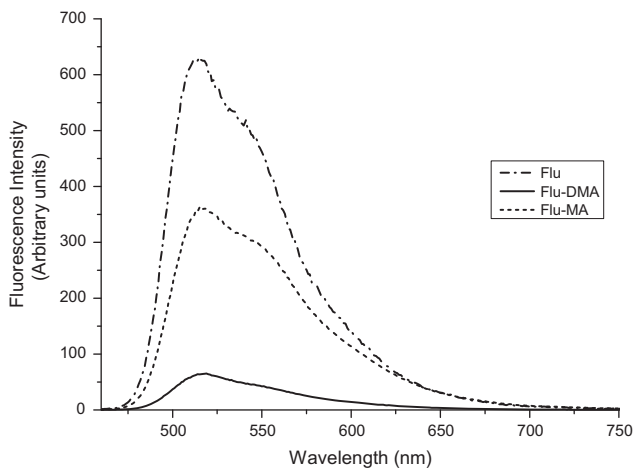


Figure 5. Fluorescence spectra of fluorescein and monomers **Flu-MA** and **Flu-DMA**.

The fluorescence spectra of the **Flu-MA** and **Flu-DMA** monomers behaved similarly showing an emission band at $\lambda_F = 519$ nm, slightly red-shifted with respect to that of fluorescein, followed by a shoulder at the same wavelength as in the previous case. Although both monomers exhibited the typical $S_0 \leftarrow S_1$ emission band of fluorescein, we can observe that the intensity of the emission band for **Flu-MA** is significantly more intense than that observed for **Flu-DMA**, which indicates a quenching effect arising from the esterification of the hydroxyl groups of this chromophore.

On the other hand, the absorption spectra of copolymers derived of **Flu-MA** are shown in Figure 6. Regardless the structure of the polymer matrix, all copolymers show a maximum absorption band around $\lambda = 494\text{--}508$ nm due to the $n\text{--}\pi^*$ transition of the fluorescein units. In the particular case of copolymers of **Flu-MA** with **EGPEA** or **EGPEM**, an additional blue-shifted band appears around $\lambda = 460\text{--}462$ nm, which is not observed in the other polymers and can be attributed to the presence of H-aggregates arising from the interaction of the phenyl units present in **EGPEA** and **EGPEM** with the fluorescein moieties. For copolymers of **Flu-MA** with **PEMEA** or **PEMEM** a small shoulder can be noticed around $\lambda = 470$ nm, which also reveals the presence of H-aggregates [40] caused by fluorescein–fluorescein interactions.

All the obtained materials containing fluorescein units showed very similar emission spectra. Figure 7 illustrates the fluorescence spectra for **poly(PEMEA)** series. As we can notice, all copolymers as well as the dispersion of fluorescein into a **poly(PEMEA)** matrix exhibited a broad emission band at $\lambda_F = 530$ nm, arising from the electronic transition $S_0 \leftarrow S_1$. This broadening that can be attributed to intermolecular fluorescein–fluorescein interactions which are highly favored in the solid state.

In general, all synthesized copolymers prepared by us showed an emission profile very close to that exhibited by fluorescein itself, with slight differences. Although the fluorescence spectra of all compounds are quite similar, in the case of the **poly(PEMEM)** series, where fluorescein units are covalently bounded to the polymer matrix, blue light emission is observed. In contrast, the sample containing dispersed fluorescein in the polymer matrix emits green light as fluorescein solutions do. This fact confirms our suspects about the presence of other species such as H-aggregates in the copolymers [31,40].

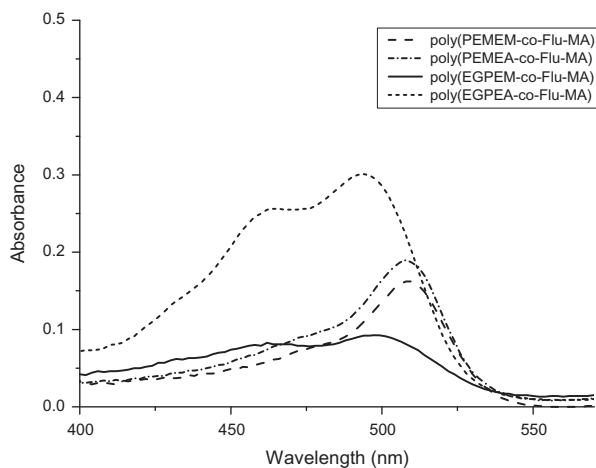


Figure 6. Absorption spectra of **poly(EGPEM-co-Flu-MA)**, **poly(EGPEA-co-Flu-MA)**, **poly(PEMEM-co-Flu-MA)**, and **poly(PEMEA-co-Flu-MA)**.

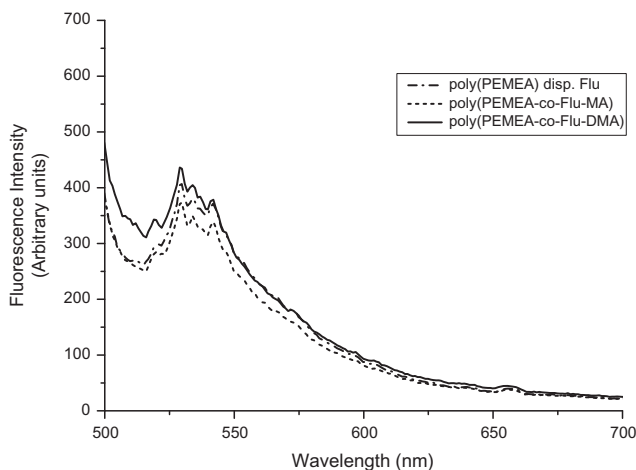


Figure 7. Fluorescence spectra of copolymers of the **poly(PEMEA)** series.

Conclusion

Four novel series of copolymers were obtained by copolymerization **Flu-MA** and **Flu-DMA** in the presence of **EGPEA**, **EGPEM**, **PEMEA** ($M_n = 475$ g/mol), and **PEMEM** ($M_n = 480$ g/mol). Although these copolymers showed to be partially soluble in some common organic solvents they were characterized by FTIR and ^1H NMR spectroscopy in gel using CDCl_3 as swelling agent. Copolymers of the **poly(EGPEA)** and **poly(EGPEM)** series showed higher stability than those of the **poly(PEMEA)** and **poly(PEMEM)** series. Their optical properties were studied by absorption and fluorescence spectroscopy in solution and in solid state. All copolymers showed a maximum absorption band around $\lambda = 494\text{--}508$ nm due to the $n\text{--}\pi^*$ transition of the fluorescein units, in some cases with the presence of shoulders indicating the presence of aggregates. Moreover, they also exhibited very similar emission spectra with a broad band at $\lambda_F = 530$ nm, whose broadening can be attributed to intermolecular fluorescein–fluorescein interactions.

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