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# Well-defined fluoro- and carbazole-containing diblock copolymers: synthesis, characterization and immobilization onto Au-coated silicon surfaces

Ioanna Savva,<sup>a</sup> Maria Demetriou,<sup>a</sup> Andreas Othonos,<sup>b</sup> Rodica Turcu,<sup>c</sup> Adriana Popa,<sup>c</sup> Sergiu Macavei<sup>c</sup> and Theodora Krasia-Christoforou<sup>\*a</sup>

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A series of well-defined diblock copolymers consisting of 2-(*N*-carbazolyl)ethyl methacrylate (CbzEMA) and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) (CbzEMA<sub>x</sub>-*b*-HFBMA<sub>y</sub>) was synthesized by Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization. All polymers were characterized in terms of molecular weights, molecular weight distributions and chemical compositions using Size Exclusion Chromatography (SEC), Fourier Transform Infrared (FTIR) spectroscopy and Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopy, respectively. The thermal properties (glass transition and decomposition temperatures) of the CbzEMA<sub>x</sub> and HFBMA<sub>x</sub> homopolymers and the CbzEMA<sub>x</sub>-*b*-HFBMA<sub>y</sub> diblock copolymers were determined by Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). As demonstrated by photoluminescence measurements, immobilization of the dithioester-ended functionalized CbzEMA<sub>x</sub>-*b*-HFBMA<sub>y</sub> chains onto Au-coated silicon surfaces has been accomplished *via* anchoring of the sulfur-containing end-groups onto the Au surfaces. The presence of the low-surface energy fluorinated block, combined with the electro-active carbazole-containing segment within CbzEMA<sub>x</sub>-*b*-HFBMA<sub>y</sub> diblock copolymers imparts to these immobilized thin layers useful properties towards their potential applicability in gas sensing technologies.

# Introduction

Polymer-based materials exhibiting electro-active functionalities have attracted significant attention due to their potential use in various optoelectronic applications including organic-based photovoltaics,<sup>1,2</sup> polymer light emitting diodes,<sup>3,4</sup> thin film transistors and sensors,<sup>5,6</sup> optical switching,<sup>7,8</sup> optical data storage and information processing.<sup>9,10</sup>

Carbazole-containing polymers belong to this class and are highly attractive due to their potential applications as photoconductors and photorefractive or charge transporting materials. Further applications of these materials include the development of light-emitting diodes (LEDs), electrochemical and gas sensors<sup>11,12</sup> and photovoltaic devices.<sup>13</sup> Carbazolyl groups easily form relatively stable radical cations (holes), present comparatively high charge carrier mobilities and exhibit high thermal and photochemical stability. Moreover, carbazole is a cheap raw material that can be very easily subjected into chemical modification reactions for the introduction of different substituents into the carbazole ring.  $^{13-16}$ 

Polymers with fluorinated groups present either in the main backbone or in the side chain, exhibit some outstanding properties, including high thermal stability, chemical inertness, low dielectric constants and dissipation factors, low water absorptivities, and good resistance to surface properties.<sup>14,17–20</sup> Due to the ability of fluoropolymers to provide a unique combination of chemical resistance, toughness, and purity, they are used in a wide variety of fluid and device handling applications.<sup>21</sup> In particular, block copolymers containing fluoropolymer segments receive considerable attention nowadays, since such materials combine the properties of the fluorocontaining segment with special characteristics deriving upon the introduction of other functional units within the copolymer.<sup>22–28</sup>

Herein, a simple and cost-effective synthetic approach involving Reversible Addition Fragmentation chain Transfer (RAFT) controlled radical polymerization<sup>29,30</sup> has been employed for the synthesis of a series of well-defined 2-(*N*-carbazolyl)ethyl methacrylate-*block*-2,2,3,3,4,4,4-heptafluorobutyl methacrylate (CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub>) diblock copolymers. For the first time HFBMA is combined with CbzEMA to yield well-defined functional diblock copolymers presenting electro-active and fluorinated moieties. Hence, the present work describes the unique combination of a rare example of a fluorinated methacrylate monomer polymerized by RAFT, with an electro- and

<sup>&</sup>lt;sup>a</sup>Department of Mechanical and Manufacturing Engineering, School of Engineering, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus. E-mail: isavva02@ucy.ac.cy; demmaria@hotmail.com; krasia@ucy.ac.cy; Fax: +357 22895081; Tel: +357 22892288 <sup>b</sup>Research Center of Ultrafast Science, Department of Physics, Faculty of Pure and Applied Sciences, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus. E-mail: othonos@ucy.ac.cy <sup>c</sup>National Institute R&D for Isotopic and Molecular Technologies, Cluj-Napoca 400293, Romania. E-mail: rodica.turcu@itim-cj.ro; adriana.popa@itim-cj.ro; sergiu.macavei@itim-cj.ro

photoactive polymethacrylate, the controlled polymerization of which has been rarely reported.<sup>31–34</sup> The RAFT process was readily employed to prepare well-defined CbzEMA<sub>x</sub> homopolymers and CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymers. The molecular and compositional characteristics of the polymers were determined by Size Exclusion Chromatography (SEC), FTIR spectroscopy and <sup>1</sup>H NMR spectroscopy respectively. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) provided information on the thermal properties (glass transition and decomposition temperatures) of these materials.

The presence of the low-surface energy fluorinated block, combined with the electro-active carbazole-containing segment within CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymers imparts to these materials useful properties for the fabrication of high quality and high performance functional thin films. In that respect, anchoring of the CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> chains onto Au-coated surfaces has been accomplished via the dithioester end groups that are retained onto the polymer chains grown by RAFT. Photoluminescence measurements demonstrated that the diblock copolymer chains have been successfully immobilized onto the Au-coated silicon surfaces. These new systems may be promising for the fabrication of novel macromolecular thin films towards gas sensing. The latter relies on the fact that ultrathin polymer films possessing electro-active moieties demonstrate enhanced performance translated into fast response, good reproducibility and high sensitivity and that the adsorption of a gas onto the surface of an electro-active polymer may cause significant changes in either the electrical or optical properties. 15,21

# **Experimental section**

# Materials

Benzene (Fluka, Merck  $\geq$  99.5%) and tetrahydrofuran (THF) (HPLC grade, LabScan) were stored over CaH<sub>2</sub> (Merck, 99.9%) and distilled under reduced pressure immediately prior to the polymerization reactions. Methanol (LabScan, Scharlau 99.9%), n-hexane (Scharlau, 99%), ethyl acetate (Scharlau, 99%), cyclohexane (Scharlau, 99%), chloroform (Scharlau, 99%), acetone (analytical grade, Scharlau), dimethylformamide (DMF) (Sigma-Aldrich,  $\geq$  99.8%), dichloromethane (Scharlau, 99%), triethylamine (Merck,  $\geq$  99.8%), hydrochloric acid (Merck, 37% solution) and diethyl ether (LabScan, 99.5%) were used as received by the manufacturer. Regarding deuterated solvents, CDCl<sub>3</sub> (Scharlau) was used in <sup>1</sup>H NMR studies. Methacryloyl chloride (Merck, ≥97%), carbazole (Sigma  $\geq$  99.5%), 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (Sigma-Aldrich, 97%), ethylene carbonate (Sigma-Aldrich, 98%), benzyl chloride (Sigma-Aldrich, 99%), α-methylstyrene (Sigma-Aldrich, 99%), sodium methoxide (Sigma-Aldrich, 30% solution in methanol), sodium hydroxide pellets (Scharlau), potassium hydroxide pellets (HiMedia, 85%), sulfur (Sigma-Aldrich, powder  $\approx 100$  mesh), anhydrous magnesium sulfate (Scharlau), sodium bicarbonate (99.5%, Sigma-Aldrich) and silica gel (Sigma-Aldrich, 60 Å, 70–230 mesh) were used as received. 2,2-Azobis(isobutylnitrile) (AIBN) (Sigma-Aldrich, 95%), was recrystallized twice from ethanol. The chain transfer agent (CTA), cumyl dithiobenzoate (CDTB), was synthesized according to a well-known procedure reported in the literature.<sup>35</sup>

#### Syntheses

2-(N-carbazolyl)ethyl methacrylate (CbzEMA). The synthesis of 2-(N-carbazolyl)ethyl methacrylate was accomplished in two steps by following a modified methodology based on previous literature reports.<sup>31,36,37</sup> 2-(N-Carbazolyl)ethanol was synthesized first and subsequently modified to generate 2-(N-carbazolyl) ethyl methacrylate. For the synthesis of 2-(N-carbazolyl)ethanol, carbazole (19.0 g, 0.114 mol) was reacted with ethylene carbonate (11.0 g, 0.125 mol) in DMF (200.0 mL) under reflux (110–130 °C) for 8 h in the presence of KOH (1.9 g, 0.034 mol). After being cooled to room temperature, the reaction mixture was filtered and then poured into a large amount of water (4.0 L). The precipitated 2-(N-carbazolyl)ethanol (white crystalline solid) was collected and dried in a vacuum furnace for 12 h at 40 °C. Subsequently, it was purified twice by recrystallization in a 1:1 benzene/cyclohexane mixture (35 mL). Recrystallization involved the dissolution of 2-(N-carbazolyl)ethanol in the above-mentioned solvent mixture under reflux and continuous stirring, followed by cooling down to room temperature and storage at -20 °C. Subsequently, the mixture was filtered off and the resulting solid (white powder) was left to dry in a vacuum furnace at room temperature.

The obtained 2-(*N*-carbazolyl)ethanol (8.5 g, 0.0403 mol), was then dissolved in dichloromethane (134.4 mL). In the reaction flask, triethylamine (6.7 mL, 0.047 mol), and methacryloyl chloride (4.7 mL, 0.047 mol) were added in a 20% excess, to ensure a more quantitative reaction. The methacryloyl chloride was added dropwise during stirring at 0 °C, (exothermic reaction). During this process, the formation of a by-product was observed as a sediment namely hydrochloric triethylamine (Et<sub>3</sub>NHCl). The reaction mixture was stirred for 24 h at room temperature. The hydrochloric triethylamine was removed from the reaction mixture by filtration.

After filtration, water (10 mL) was added for the hydrolysis of the excess of methacryloyl chloride into methacrylic acid. The methacrylic acid resigned into the aqueous phase whereas the product remained in the organic phase.

Subsequently, dichloromethane (40.0 mL) was added in the solution and the mixture was extracted two times with water (5.0 and 10.0 mL), then three times with NaHCO<sub>3</sub> solution (5% in water, addition of 5.0 mL each time) and again three times with water. After the extractions, anhydrous MgSO<sub>4</sub> was added in the organic phase in order to remove the water traces. Subsequently, the organic solvent was removed under reduced pressure; the product was dried and recrystallized twice in methanol. The recrystallization process was carried out at room temperature, in order to avoid thermal polymerization of the monomer. The resulting solid was then filtered and dried in a vacuum furnace at room temperature. The synthetic route followed for the synthesis of the CbzEMA monomer is presented in Fig. 1, whereas the chemical structure of the monomer is depicted in Fig. 2.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.1–8.0 (br, 2H (e)), 7.5–7.34 (m, 6H (f)), 5.92–5.85 (br, 1H (b<sub>1</sub>)), 5.48–5.44 (br, 1H (b<sub>2</sub>)), 4.62–4.52 (m, 4H (c, d)), 1.8 (s, –CH<sub>3</sub> (a)).



Fig. 1 Two-step synthetic methodology followed for the preparation of the 2-(N-carbazolyl)ethyl methacrylate (CbzEMA).

# Poly(2-(N-carbazolyl) ethyl methacrylate) (CbzEMA<sub>x</sub>)

A series of well-defined CbzEMA<sub>x</sub> homopolymers, with various polymerization degrees (DP), was prepared by RAFT. To a round-bottom flask (25.0 mL) maintained under a dry nitrogen atmosphere, CbzEMA (1 g,  $3.58 \times 10^{-3}$  mol) was added. CDTB ( $8.12 \text{ mg}, 2.98 \times 10^{-5}$  mol) and AIBN ( $2.68 \text{ mg}, 1.63 \times 10^{-5}$  mol) were dissolved in freshly distilled THF (2.0 mL) and were transferred into the flask with the aid of a syringe. Subsequently, the resulting solution was degassed by three freeze-evacuate-thaw cycles, placed under a dry nitrogen atmosphere and heated in a thermostated oil bath at 63 °C for 18 h. The polymerization was terminated by cooling the reaction down to room temperature. The produced CbzEMA<sub>x</sub> (0.634 g, 64% polymerization yield) (Fig. 3) was retrieved by precipitation in *n*-hexane and was left to dry *in vacuo* at room temperature for 24 h.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.9 (br, 2H (e)), 7.22–7.07 (m, 6H (f)), 4.3–3.6 (m, br 4H (c, d)), 1.85 (br,  $-CH_2$  (b)), 0,8–1.0 (br,  $-CH_3$  (a)).

# Poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (HFBMA<sub>x</sub>)

To a round-bottom flask (50.0 mL) maintained under a dry nitrogen atmosphere, HFBMA (3.0 mL,  $1.5 \times 10^{-2}$  mol) was added. CDTB (20.5 mg,  $7.52 \times 10^{-5}$  mol) and AIBN (5.53 mg,  $3.37 \times 10^{-5}$  mol) were dissolved in freshly distilled THF (12.0 mL) and were transferred into the flask with the aid of a syringe. Subsequently, the resulting solution was degassed by three freeze-evacuate-thaw cycles, placed under a dry nitrogen atmosphere and heated in a thermostated oil bath at 63 °C for 18 h. The polymerization was terminated by cooling the reaction down to room temperature. The produced HFBMA<sub>x</sub> (1.6974 g, 42% polymerization yield) (Fig. 4) was retrieved by precipitation in methanol and was left to dry *in vacuo* at room temperature for 24 h. Further purification, of the polymer was carried out by reprecipitation in *n*-hexane.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.5–4.3 (s, br, 2H (g)), 1.95 (br, 2H (b')), 1.10 (br, –CH<sub>3</sub> (a')).



**Fig. 2** The chemical structure of the 2-(*N*-carbazolyl)ethyl methacrylate (CbzEMA) monomer.



Fig. 3 The chemical structure of the poly(2-(N-carbazolyl)) ethyl methacrylate) (CbzEMA<sub>x</sub>) homopolymer.

#### **Diblock copolymers**

Poly[2-(*N*-carbazolyl)ethyl methacrylate]-*block*-poly[(2,2,3,3,4,4,4-heptafluorobutyl methacrylate)] (CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub>). To a round-bottom flask (25.0 mL) maintained under a dry nitrogen atmosphere, AIBN (1.45 mg,  $8.85 \times 10^{-6}$  mol) and CbzEMA<sub>x</sub> (0.626 g,  $\tilde{M}_n = 31$  711 g mol<sup>-1</sup>, 2.24 × 10<sup>-3</sup> mol, macro-CTA) dissolved



**Fig. 4** The chemical structure of the poly(2,2,3,3,4,4,4)-heptafluorobutyl methacrylate) (HFBMA<sub>x</sub>) homopolymer.



**Fig. 5** The chemical structure of the  $CbzEMA_x$ -*b*-HFBMA<sub>y</sub> diblock copolymers.

in freshly distilled THF (4.0 mL) were placed together with HFBMA (0.5 mL,  $2.51 \times 10^{-3}$  mol). The reaction mixture was degassed by three freeze-evacuate-thaw cycles, placed under a dry nitrogen atmosphere and heated in a thermostated oil bath at 63 °C for 18 h. The polymerization was terminated by cooling the reaction down to room temperature. The produced CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymer (0.881 g, 38% polymerization yield) (Fig. 5) was retrieved by precipitation in *n*-hexane or methanol and was left to dry *in vacuo* at room temperature for 24 h.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.9 (br, 2H (e)), 7.21–7.06 (br, 6H, (f)), 4.41–4.3 (s, br, 2H (g)), 4.3–4.05 (br, 2H (c)), 4.05–3.75 (br, 2H (d)), 1.95 (br, -CH<sub>2</sub> (b, b')), 1.0–1.2 (br, -CH<sub>3</sub> (a, a')).

#### **Film fabrication**

Polymer films were generated on gold-coated silicon substrates (gold film thickness 25 nm) upon immersion of the latter in a

room temperature.<sup>38</sup> After 24 h, the solution was removed *via* a syringe and the substrate with adsorbed polymer was washed with fresh solvent (THF) until no polymer could be detected by UV-vis analysis in the washing medium. The films were then left to dry on the bench for 24 h and were not supplementary dried prior to photoluminescence and atomic force microscopy (AFM) measurements.

## Instrumentation

Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopy was used for confirming the expected chemical structure of the polymers. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using an Avance Brucker 300 MHz spectrometer equipped with an Ultrashield magnet. The CDCl<sub>3</sub> contained traces of tetramethyl-silane (TMS), which was used as an internal reference. For classifying the signals in the <sup>1</sup>H NMR spectra, abbreviations such as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad) are used.

The molecular weights and polydispersity indices of the polymers were determined by Size Exclusion Chromatography (SEC). All measurements were carried out at room temperature using Styragel HR 3 and Styragel HR 4 columns. The mobile phase was THF, delivered at a flow rate 1 mL min<sup>-1</sup> using a Waters 515 isocratic pump. The refractive index was measured with a Waters 2414 refractive index detector. The instrumentation was calibrated using poly(methyl methacrylate) (PMMA) standards with narrow polydispersity indices (MWs of 102, 450, 670, 1580, 4200, 14 400, 31 000, 65 000, 126 000, 270 000, 446 000, 739 000 g mol<sup>-1</sup>) supplied by Polymer Standards Service (PSS).

The refractive index of THF, a HFBMA<sub>x</sub> homopolymer and a CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymer was determined using an ABBE refractometer.

Differential Scanning Calorimetry (DSC) was used to measure the glass transition temperatures ( $T_g$ ) of the homopolymers and the diblock copolymers using a Q100 TA Instrument with a heating rate of 10 °C min<sup>-1</sup>. Each sample was scanned twice between -100 °C to +170 °C. The second run (heat) was used for data analysis.

Thermal Gravimetric Analysis (TGA) measurements were used in order to determine the thermal stability of the polymers and they were based on continuous measurement of weight on a sensitive balance (thermobalance) upon temperature increase. TGA measurements were performed on a Q-500 TA Instrument under an argon flow at heating rate of 10  $^{\circ}$ C min<sup>-1</sup>.

Ultra Violet-visible spectroscopy (UV-vis) was carried out on a Jasco UV-vis spectrophotometer (V 630). Measurements were performed in THF and solution concentration was approximately  $1 \text{ g L}^{-1}$ .

Fourier Transform Infrared Spectroscopy (FTIR) was carried out on a Jasco FTIR spectrometer (4100).

The AFM investigations have been performed with an UHV-3500 Scanning Probe Microscope from RHK Technology. The system is operating in ultra high vacuum (UHV) and the samples were analyzed in the non-contact operating mode using a scan speed of 2.71 micrometer/s and a tip frequency of 74.7 kHz. n-Type silicon (phosphorus doped) tips with a conical shape were used to acquire the AFM images. Photoluminescence (PL) measurements were performed using a UV source based on a Ti-sapphire ultrafast laser generating 75 fs pulses at repetition rate of 250 kHz. In this system the fundamental light at 800 nm generated by the ultrafast amplifier was frequency doubled and used as the source of excitation for an Optical Parametric Amplifier (OPA) which was tuned for these experiments at 510 nm. The OPA pulses were frequency doubled using a BBO non-linear crystal to produce 255 nm. The UV beam was then separated and directed on the sample using several wavelength selective dielectric mirrors. The average power that was incident on the sample was approximately 10  $\mu$ W with a measured spot size at the excitation region of 2 mm. The PL emission was collected and analyzed through a double pass spectrometer equipped with a photon counting photomultiplier system.

The gold-coated silicon substrates used (Au film thickness: 25 nm) were prepared by sputtering using argon at a pressure of approximately  $10^{-2}$  mBar.

# **Results and discussion**

#### Molecular characterization

Well-defined CbzEMA<sub>x</sub> and HFBMA<sub>x</sub> homopolymers and CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymers were successfully synthesized following typical RAFT methodologies already described in the Experimental Section. The molecular characterization of these materials was carried out by means of SEC, <sup>1</sup>H NMR and FTIR. Table 1 summarizes the chemical structures of all homopolymers and diblock copolymers prepared in this study along with their molecular weight (MW) and compositional characteristics.

<sup>1</sup>H NMR spectroscopy confirmed the expected chemical structure of the diblock copolymers. In Fig. 6 the <sup>1</sup>H NMR spectrum of the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> diblock copolymer is exemplarily given. The peak assignments are shown in the spectrum. The degrees of the polymerization of the HFBMA comonomer were determined from the ratio of the areas under the characteristic signals of the CbzEMA and HFBMA, appearing at 4.2–3.9 ppm (c, d) and 4.4 ppm (g) respectively. The signal at 4.4 ppm corresponds to the methylene protons

**Table 1**Characteristics of the homopolymers and diblock copolymersbased on CbzEMA and HFBMA obtained by RAFT (polymerizationyields, molecular weights and polydispersity indices)

Polymer <sup>a</sup>	Yield $(\%)^b$	SEC Results <sup>c</sup>		
		$\bar{M}_{\rm n}$	$ar{M}_{ m w}$	PDI
CbzEMA <sub>13</sub>	58	3602	4174	1.16
HFBMA <sub>95</sub>	42	25 861	32 283	1.25
CbzEMA <sub>13</sub> -b-HFBMA <sub>244</sub>	52	25 437	32 623	1.28
CbzEMA <sub>13</sub> -b-HFBMA <sub>316</sub>	80	25 781	31 440	1.22
CbzEMA <sub>52</sub> -b-HFBMA <sub>69</sub>	n.d.	22 106	35 105	1.59
CbzEMA <sub>113</sub> -b-HFBMA <sub>52</sub>	38	34 245	43 406	1.26

<sup>*a*</sup> Determined by SEC and <sup>1</sup>H NMR. <sup>*b*</sup> [(g monomer)/(mol RAFT agent)] × (polymerization yield) + MW of CTA (for homopolymers) and [(g monomer)/(mol macro-CTA agent)] × (polymerization yield) +  $\bar{M}_n$  of macro-CTA (for diblock copolymers). <sup>*c*</sup> SEC calibrated with PMMA standards;  $\bar{M}_n$  = number average molecular weight; PDI = polydispersity index; CbzEMA = 2-(*N*-carbazolyl) ethyl methacrylate; HFBMA = 2,2,3,3,4,4,4-heptafluorobutyl methacrylate; n.d.: not determined.



Fig. 6  $^{1}$ H NMR spectrum of the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> diblock copolymer. \*Solvent (CHCl<sub>3</sub>).

adjacent to the oxygen of the ester group in HFBMA.<sup>39,40</sup> The signals appearing at 4.2–3.9 ppm correspond to the –CH<sub>2</sub>–CH<sub>2</sub>– protons of the carbazole group (adjacent to nitrogen in CbzEMA).<sup>41</sup>

Moreover, FTIR spectroscopy was employed to verify the chemical structure of the polymers. Fig. 7 presents the FTIR spectra of the HFBMA<sub>95</sub> and CbzEMA<sub>52</sub> homopolymers and of the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> diblock copolymer. In the spectra the vibration bands appearing at 1597 cm<sup>-1</sup> correspond to the C=O bond that is present in the systems<sup>42</sup> whereas the vibration frequency of the C–O bond of the ester group appears at 1731 cm<sup>-1</sup>. In the FTIR spectrum of the HFBMA<sub>95</sub> homopolymer, the signal appearing at 1351 cm<sup>-1</sup> corresponds to the vibration frequency of the C–F bond. Moreover, the two signals at 1203 cm<sup>-1</sup> and 1156 cm<sup>-1</sup>, correspond to the symmetric and antisymmetric stretching vibrations of the –CF<sub>2</sub> group respectively, whereas two medium bands appear at 749 cm<sup>-1</sup> and 722 cm<sup>-1</sup>, corresponding to a combination of cocking and wagging vibrations of the –CF<sub>3</sub> group.<sup>40</sup>

The average MWs and PDIs of the homopolymers and corresponding diblock copolymers were determined by SEC. All data are provided in Table 1. All polymers (with the exception of the CbzEMA<sub>52</sub>-*b*-HFBMA<sub>69</sub> system) exhibited low PDI (<1.3), which are well-comparable with PDI values of previously reported polymers prepared by RAFT,<sup>29</sup> demonstrating the well-defined character of these new materials.

Fig. 8(a) displays the SEC traces of the HFBMA<sub>95</sub> and CbzEMA<sub>108</sub> homopolymers, and of the CbzEMA<sub>113</sub>*b*-HFBMA<sub>52</sub> and CbzEMA<sub>13</sub>-*b*-HFBMA<sub>244</sub> diblock copolymers. Due to the lower refractive index of the HFBMA<sub>95</sub> homopolymers compared to that of THF, the signal corresponding to the SEC eluogram of the HFBMA<sub>95</sub> homopolymer and CbzEMA<sub>13</sub>-*b*-HFBMA<sub>244</sub> diblock copolymer is negative. As provided in Table 2, the experimental refractive index value corresponding to the HFBMA<sub>95</sub> homopolymer was determined



**Fig. 7** The FTIR spectra of the HFBMA<sub>95</sub> and CbzEMA<sub>52</sub> homopolymers, and the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> diblock copolymer.

to be 1.4065, which is lower than that of THF. In contrary, the refractive index of the CbzEMA<sub>113</sub>-b-HFBMA<sub>52</sub> diblock copolymer was determined to be higher than that of the pure solvent as expected, due to the higher content of the CbzEMA units within the diblock copolymer.

In Fig. 8(b) the SEC traces of the CbzEMA<sub>13</sub> homopolymer and the CbzEMA<sub>13</sub>-*b*-HFBMA<sub>244</sub> diblock copolymer are illustrated. As seen in the Figure, the molecular weight distribution (MWD) of the latter is shifted towards higher MWs compared to that of the corresponding homopolymer, demonstrating the block efficiency from homopolymer to block copolymer.

#### Thermal properties

DSC and TGA measurements were carried out for the determination of the glass transition  $(T_g)$  and decomposition temperatures of the polymers, respectively. The glass transition temperature  $(T_g)$  of CbzEMA<sub>52</sub> and HFBMA<sub>95</sub> prepared by RAFT was 142 and 52 °C respectively (Fig. 9(a)) which is close to literature values.<sup>43,44</sup> The diblock copolymers exhibited two  $T_g$ s, at ~128 °C (corresponding to the CbzEMA<sub>x</sub> block) and ~58 °C (corresponding to the HFBMA<sub>y</sub> block). These results may suggest that the CbzEMA<sub>x</sub>-b-HFBMA<sub>y</sub> diblock copolymers tend to microphase separate in the bulk. As far as thermal stability is concerned, all polymers start losing weight at ~300–350 °C and decompose losing most of their weight between 400–450 °C as indicated by TGA (Fig. 9(b)).

### Film fabrication and characterization

As already described in the experimental section, a polymer layer was generated on a gold-coated silicon substrate upon immersion of the latter in a dilute THF solution of CbzEMA<sub>52</sub>-*b*-HFBMA<sub>69</sub> at room temperature. The strong specific interaction between the sulfur atom and the gold surface<sup>45</sup> induced the spontaneous assembly of the polymer chains onto the gold interface as schematically presented in Fig. 10.

According to C.-A. Fustin and A.-S. Duwez,<sup>46</sup> the dithioester group is chemisorbed on a gold substrate with both sulfur atoms



**Fig. 8** SEC eluograms of (a) HFBMA<sub>95</sub> and CbzEMA<sub>108</sub> homopolymers and of the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> and CbzEMA<sub>13</sub>-*b*-HFBMA<sub>244</sub> diblock copolymers and (b) CbzEMA<sub>13</sub> homopolymer and the CbzEMA<sub>13</sub>-*b*-HFBMA<sub>244</sub> diblock copolymer.

attached onto its surface, forming monolayers, whereas based on X-ray photoelectron spectroscopy (XPS) data the formation of multilayers is excluded.

Prior to photoluminescence measurements (PL) performed on the polymer-coated Au-silicon substrates, UV-Vis characterization of the homopolymers and diblock copolymers was carried out in THF. In Fig. 11 the UV-Vis spectra of (i) the CbzEMA<sub>52</sub> and HFBMA<sub>95</sub> homopolymers and (ii) the CbzEMA<sub>113</sub>*b*-HFBMA<sub>52</sub> diblock copolymer recorded in THF at room temperature are shown. Several absorption maxima appear in the spectra of the CbzEMA<sub>52</sub> and CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> within the wavelength range of 240–350 nm with the strong

**Table 2** Refractive index of HFBMA95 homopolymer, CbzEMA113-b-HFBMA52 diblock copolymer and THF

Polymer	Refractive Index		
THF	1.4080		
HFBMA <sub>95</sub>	1.4065		
CbzEMA <sub>113</sub> - <i>b</i> -HFBMA <sub>52</sub>	1.4135		

intense band at around 300 nm being assigned to the  $\pi$ - $\pi$ \* local excitation of carbazole moieties, whereas HFBMA<sub>95</sub> presents an absorption band in the UV region.

Room temperature photoluminescence (PL) measurements were carried out on the Au-coated silicon substrates prior and after the immersion of the latter in the polymer solution for 24 h, in order to verify the anchoring of the polymers onto the Au surfaces. Fig. 12(a) presents the PL emission spectra recorded in the absence and presence of anchored polymer chains after 24 h immersion of the substrates in the polymer solution. Furthermore, time resolved PL at the peak of the signal (*i.e.* at 450 nm) is presented in Fig. 12(b). Clearly seen from the data, the Au appears to have almost zero PL whereas the CbzEMA<sub>52</sub>-b-HFBMA<sub>69</sub> PL emission is much stronger under identical excitation conditions and depends on the sample position (see PL for spot 1 and spot 2).

It is noteworthy to emphasize at this point that the spectral profile is the same over the entire sample. The observed differences in the intensity of the signal at different positions onto the sample may suggest that the polymer is not evenly distributed onto the substrate. The latter has been confirmed by



Fig. 9 (a) DSC thermograms for the HFBMA<sub>95</sub> and CbzEMA<sub>52</sub> homopolymers and the CbzEMA<sub>113</sub>-b-HFBMA<sub>52</sub> diblock copolymer (b) TGA curves of the CbzEMA<sub>52</sub> and HFBMA<sub>95</sub> homopolymers and the CbzEMA<sub>113</sub>-b-HFBMA<sub>52</sub> diblock copolymer.



Fig. 10 Schematic representation of the generation of a polymer film on gold-coated silicon substrate.

AFM characterization of the resulting films. Fig. 13 shows the AFM measured surface features of the analyzed films covering an area of 250 nm  $\times$  250 nm and 500 nm  $\times$  500 nm. The change of colors over the image indicates the thickness variation. The

heights of the surface features are represented with the brighter pixel whereas the dark pixel indicates the valleys. As shown in Fig. 13, the distribution of the polymer onto the substrate is uneven. The polymer film roughness varies between 6 and 12 nm.



**Fig. 11** UV-vis spectra of the CbzEMA<sub>52</sub> and HFBMA<sub>95</sub> homopolymers and the CbzEMA<sub>113</sub>-*b*-HFBMA<sub>52</sub> diblock copolymers recorded in THF.

In the case of the Au-coated silicon substrate covered with polymer chains it is clearly observed that the "monomer" emission peaks appearing at 348 and 365 nm in the case of the CbzEMA<sub>x</sub> homopolymers<sup>47</sup> do not exist, whereas an emission peak at ~435 nm appears instead. In general as stated by Keyanpour-Rad et al.,47 the fluorescence emission expected for "monomer" emission is a mirror image of the  ${}^{1}L_{h} \leftarrow {}^{1}A$ absorption band, resulting from the singlet state of an excited carbazolyl chromophore that does not interact strongly with a neighbouring chromophore. It is likely that the anchoring of the dithioester-functionalized CbzEMA<sub>52</sub>-b-HFBMA<sub>69</sub> diblock copolymer chains onto the Au surface resulted in the generation of a parallel overlap interchromophore geometry allowing for excimer formation to occur. Similarly, Keyanpour-Rad and coworkers have demonstrated the excimer formation in solution at different  $\lambda_{max}$  excimer wavelengths ranging between 418–440 nm (depending on the solvent system used) for a polymethacrylate containing side-chain electroactive carbazole moiety namely poly([2-(9-ethyl)carbazolyl]methyl methacrylate), due to favourable



Fig. 12 (a) PL spectra of Au-coated silicon substrate and CbzEMA<sub>52</sub>-*b*-HFBMA<sub>69</sub> -S-C=S-/Au-coated silicon substrate (recorded at different sample positions). (b) Time resolved PL at the peak of the signal (*i.e.* at 450 nm).



Fig. 13 AFM 3D-graph topography images of a gold substrate immersed in a THF solution of CbzEMA<sub>52</sub>-b-HFBMA<sub>69</sub> (2 g L<sup>-1</sup>) at room temperature for 24 h.



Fig. 14 AFM 3D-graph topography images of a gold substrate immersed in a THF solution of CbzEMA<sub>52</sub>-*b*-HFBMA<sub>69</sub> (2 g  $L^{-1}$ ) at room temperature for 48 h.

steric constrains. Moreover, it has been found that the latter becomes much more pronounced when the polymer chain is immobilized in a rigid matrix.<sup>47</sup>

For applications involving gas sensing and optoelectronics it is of paramount importance to use active surfaces characterized by uniformity and homogeneity. Examples appearing in the literature reporting on the effect of film thickness on gas sensing properties<sup>48</sup> and optoelectronic behavior<sup>49</sup> support the abovementioned. V. Koutsos and co-workers have investigated the structural regimes of thiol-end-functionalized polystyrene monolayers by means of scanning force microscopy.<sup>50</sup> Upon using longer incubation times *i.e.* exposing the gold-coated substrates to polymer solutions for longer time periods, higher surface coverage is obtained. The latter significantly affected the morphology adopted by the collapsed polymer chains onto the surface. Consequently, in an effort to improve the film uniformity, new samples were prepared upon immersing the gold-coated silicon substrates in the polymer solution for 48 h. AFM characterization of the resulting films (Fig. 14) indicated the generation of monolayers characterized by higher uniformity. However, a more systematic investigation toward this direction is required for obtaining films of high quality, allowing the future exploitation of these materials in gas sensing and optoelectronic applications.

# Conclusions

In the present work, well-defined diblock copolymers consisting of 2-(*N*-carbazolyl)ethyl methacrylate (CbzEMA) and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) units have been successfully synthesized and characterized in regards to their molecular characteristics and thermal properties. Due to the presence of dithioester end-groups onto the diblock copolymer chains generated by RAFT controlled radical polymerization, their immobilization onto Au-coated silicon substrates has been accomplished *via* anchoring of the sulfurcontaining end-groups onto the Au surfaces. The PL data revealed that excimer formation occurs suggesting that the immobilization of the polymer chains onto the Au-coated silicon substrate may assist their arrangement into a parallel geometry, allowing for interchromophore overlapping and thus excimer generation. The combination of a low-surface energy fluorinated block, with an electro-active carbazole-containing segment imparts to these immobilized thin layers useful properties towards their potential applicability in gas sensing technologies.

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