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ORIGINAL PAPER

Novel regioregular poly(3-hexylthiophene)-based polycationic block copolymers

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Abstract Regioregular poly(3-hexylthiophene) has been successfully incorporated into various poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-based block copolymers, i.e., P3HT-*b*-PDMAEMA, via Grignard metathesis (GRIM) method and atom transfer radical polymerization (ATRP) reactions. The structure of the diblock copolymers was fully confirmed by FT-IR, ^{1}H NMR spectroscopy, gel permeation chromatography (GPC), and ultraviolet–visible spectroscopy (UV–vis). The recovered copolymers could be treated by protonation of the pending tertiary amine functions and depending on the relative content in PDMAEMA, the copolymers could be solubilized in more polar solvents where P3HT alone proved to be totally insoluble.

Keywords Poly(3-hexylthiophene) · Poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) · ATRP · Block copolymer

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Introduction

Among semiconducting polymers, poly(3-alkylthiophene)s have attracted great attention and generated many studies over the past decade. Among them, regioregular (head-to-tail) poly(3-hexylthiophene) has been especially investigated due to its superior opto-electronic properties, good solubility in the most common organic solvents, chemical and thermal stabilities and also very low toxicity [1–4]. These properties enable regioregular poly(3-hexylthiophene) (P3HT) to be significantly useful in a large variety of applications such as optical sensors, smart windows, organic field effect transistors (OFETs), electrochromic devices, and solar cells [5–9]. Since both Mc Cullough et al. and Yokozawa et al. discovered and, respectively, improved the Grignard metathesis polymerization (GRIM) of 3-alkylthiophene derivatives, various block copolymers have been synthesized leading to unique and attractive combination of nanostructure formation and electronic behavior [10–15]. The combination of conjugated and non-conjugated segments generates interesting materials expecting to phase-segregate and leads to the formation of nanoscale morphologies owing to the immiscibility of the covalently connected blocks [16].

Rod-coil block copolymers containing P3HT or other conjugated polymers have already been reported by some research groups. As an example, McCullough and his coworkers have recently reported on the synthesis and morphological characterization of di- and triblock copolymers containing regioregular P3HT. After adequate end-group(s) derivatization, the telechelic regioregular poly(3-hexylthiophene) was employed as macroinitiator in atom transfer radical polymerization (ATRP) of styrene, methyl acrylate (MA), or methyl methacrylate (MMA) monomers [17]. The emergence of in situ end-group functionalization (taking advantage of the quasi-living GRIM) has also provided another synthetic procedure for the preparation of alkenyl-terminated regioregular P3HT in a one-pot reaction. Further chemical modification of allyl or vinyl end-groups by hydroboration/oxidation reaction, followed by the conversion into bromoester, allowed for the synthesis of diblock copolymers such as poly(3-hexylthiophene)-*block*-poly(methyl acrylate), poly(3-hexylthiophene)-*block*-poly(tert-butyl methacrylate), and poly(3-hexylthiophene)-*block*-poly(isobornyl methacrylate) [18].

Interestingly, the preparation of amphiphilic block copolymers, constituted by a rigid conductive poly(3-hexylthiophene) and hydrophilic flexible block was also achieved [19–24]. Similarly, ionic or non-ionic polymers have been grafted along the conjugated backbone to achieve water soluble graft copolymers. Conjugated polyelectrolytes have been developed as highly sensitive sensors for electronic devices such as organic field-effect transistors as well as for biological targets [25]. Recently, Winnik et al. have reported the synthesis of a water soluble and pH-responsive brush-like copolymer composed by a polythiophene backbone and poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (PDMAEMA) side chains [26]. This graft copolymer exhibits a reversible response to pH changes in water. However, the polythiophene backbone of this graft copolymer was synthesized by oxidative process leading to non regioregular P3HT with uncontrolled molecular weight and high polydispersity index.

Herein, we report an easy way to produce rod-coil amphiphilic poly(3-hexylthiophene)-*block*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) block copolymers by a perfectly controlled five-step synthetic strategy taking advantages of both GRIM and ATRP processes.

Experimental section

Materials

3-Hexylthiophene, *N*-bromosuccinimide, iodine, iodobenzene diacetate were purchased from Acros and used as received. Ni(dppp)Cl_2, i-PrMgCl in THF (2 mol/l) were also purchased from Acros and stored in glove box at room temperature. 2-Bromoisobutyryl bromide (Br-iBuBr), triethylamine (NEt_3, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), anhydrous *N*,*N*-dimethylformamide (DMF, 99.8%), sodium borohydride ($NaBH_4$, 99%), and phosphorus(V) oxychloride ($POCl_3$, 99%) were purchased from Aldrich. Copper(I) bromide (CuBr, 98%) was purchased from Fluka and used without further purification. *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA) (Aldrich, 98%) was distilled under vacuum and stored under nitrogen at −20 °C. Chloroform ($CHCl_3$, Labscan, 99%), toluene (Labscan, 99%), tetrahydrofuran (THF, Labscan 99%) were dried using an MBraun solvent purification system under N_2. Dichloromethane (Chem-Laboratory, 99.8%), heptane (Labscan, 99%), hexane (Labscan, 99%), and methanol (Chem-Laboratory, 99.8%) were used as received. All reactions were performed in oven-dried glassware under purified nitrogen atmosphere.

Synthesis of 2-bromo-3-hexylthiophene (**2**)

To a solution of 3-hexylthiophene (5 g, 29.7 mmol), anhydrous THF (50 mL) in a 200 mL flask, a solution of *N*-bromosuccinimide (5.29 g, 29.7 mmol) was added slowly at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h. Then, 50 mL of distilled water was added to the reaction mixture, and the mixture was extracted with diethyl ether. The organic layer was washed with a solution of $Na_2S_2O_3$ (10%), with a solution of KOH (10%) and finally dried over anhydrous $MgSO_4$. The mixture was distilled to give a colorless oil. (6.7 g, 92%).^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):7.19 (d, 1H), 6.82 (d, 1H), 2.59 (t, 2H), 1.59 (quint, 2H), 1.33 (m, 6H), 0.91 (t, 3H). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 141.0, 128.2, 125.1, 108.8, 31.6, 29.7, 29.4, 28.0, 22.6, 14.1.

Synthesis of 2-bromo-3-hexyl-5-iodothiophene (**3**)

Iodine (1.42 g, 11.18 mmol) and iodobenzene diacetate (1.965 g, 6.1 mmol) were added to a solution of 2-bromo-3-hexylthiophene (2.5 g, 10.1 mmol) in dichloromethane (25 mL) at 0 °C. The mixture was stirred at room temperature for 4 h. Then, aqueous $Na_2S_2O_3$ (10%) was added, and the mixture was extracted with diethyl ether and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain the crude product. The residue was purified by silica column chromatography (eluent:heptane) to give pure 2-bromo-3-hexyl-5-iodothiophene as pale yellow oil. (3.0 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.97 (s, 1H), 2.52 (t, 2H), 1.56 (quint, 2H), 1.32 (m, 6H), 0.89 (t, 3H). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 144.3, 137.0, 111.7, 71.0, 31.5, 29.6, 29.2, 28.8, 22.5, 14.1.

Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with H/Br end groups (**4**)

A dried 500 mL three-neck flask was flushed with nitrogen and was charged with 2-bromo-3-hexyl-5-iodothiophene (15 g, 40 mmol). After three azeotropic distillations by toluene, anhydrous THF (220 mL) was added under nitrogen atmosphere, the mixture was stirred at 0 °C for 1 h. i-PrMgCl (2 M solution in THF, 19.14 mL, 38.28 mmol) was added via a syringe and the mixture was continuously stirred at 0 °C for 1 h. The reaction mixture was allowed to cool down to 0 °C. The mixture was transferred to a flask containing a suspension of Ni(dppp)Cl_2 (760 mg, 1.4 mmol) in THF (25 mL). The polymerization was carried out for 24 h at 0 °C followed by fast addition of a 5 M HCl solution. The reaction was stirred for 15 min and extracted with chloroform. The polymer was precipitated from cold methanol and washed several times with hexane. The polymer was characterized by ^{1}H NMR and GPC. Yield: 70%.

FT-IR (cm^{-1}): 721, 819, 1376, 1454, 1510, 2853, 2922, 2953, 3056. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.96 (s, 1H), 2.90 (t, 2H), 1.79 (q, 2H), 1.52 (q, 6H), 0.94 (t, 3H). GPC, M_n, 6000 g/mol. PDI, 1.18.

Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with CHO/Br end groups (**5**)

Polymer **4** (1 g) was dissolved in 260 mL of anhydrous toluene under nitrogen. *N*,*N*-dimethylformamide (DMF) (5.12 mL, 66.3 mmol) and phosphorus(V) oxychloride ($POCl_3$) (5.30 mL, 58 mmol) were then added to the solution. The reaction was performed at 75 °C for 24 h. The solution was cooled down to room temperature, followed by the adding of saturated aqueous solution of sodium acetate. The solution was stirred for 4 h. Then, the polymer was extracted with chloroform. The polymer was precipitated from cold methanol and washed with cold hexane and dried in vacuum. Yield: 93%. FT-IR (cm^{-1}): 721, 819, 1376, 1453, 1509, 1649, 2854, 2923, 2953, 3056. ^{1}H NMR (300 MHz, $CDCl_3$); δ (ppm): 9.99 (s, 1H), 6.96 (s, 1H), 2.78 (t, 2H), 1.69 (q, 2H), 1.49 (q, 6H), 0.89 (t, 3H).

Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with CH_2OH/Br end groups (**6**)

Polymer **5** (500 mg, 8.33×10^{-5} mol) was dissolved in 30 mL of anhydrous THF under nitrogen. $NaBH_4$ (41.8 mg, 1.1×10^{-3} mmol) was then added. The mixture was kept stirring at room temperature for 2 h. Then, the solvent was evaporated under vacuum. The polymer was precipitated from cold methanol. After drying in vacuum, 480 mg of polymer was obtained. Yield: 96%. FT-IR (cm^{-1}): 724, 817, 1376, 1453, 1509, 1561, 2853, 2922, 2953, 3056. ^1H NMR (300 MHz, $CDCl_3$); δ (ppm): 6.96 (s, 1H), 4.8 (s, 2H), 2.78 (t, 2H) 1.69 (q, 2H), 1.49 (q, 6H), 0.89 (t, 3H).

Synthesis of bromoester-terminated poly(3-hexylthiophene) (P3HT-Macroinitiator) (**7**)

Polymer **6** (480 mg, 83.3×10^{-5} mol) was dissolved in 20 mL of anhydrous THF under nitrogen. To this solution triethylamine (NEt_3) (1 mmol) and 2-bromoisobutyryl bromide (0.83 mmol) were added. Then the reaction was carried out at 50 °C overnight, the polymer was extracted by chloroform. The solution was washed twice with distilled water. The polymer was precipitated from cold methanol. After drying in vacuum, 475 mg of polymer was obtained. Yield: 95%. FT-IR (cm^{-1}): 724, 818, 1376, 1451, 1509, 1561, 1735, 2853, 2922, 2953, 3056. ^1H NMR (300 MHz, $CDCl_3$); δ (ppm): 6.96 (s, 1H), 5.29 (s, 2H), 2.78 (t, 2H), 1.93 (t, 6H), 1.69 (q, 2H), 1.49 (q, 6H), 0.89 (t, 3H). GPC, 6000 g/mol. PDI, 1.23.

Synthesis of poly(3-hexyl thiophene)-*b*-poly(*N*,*N*-dimethylaminoethyl methacrylate) (P3HT-*b*-PDMAEMA) (**8**)

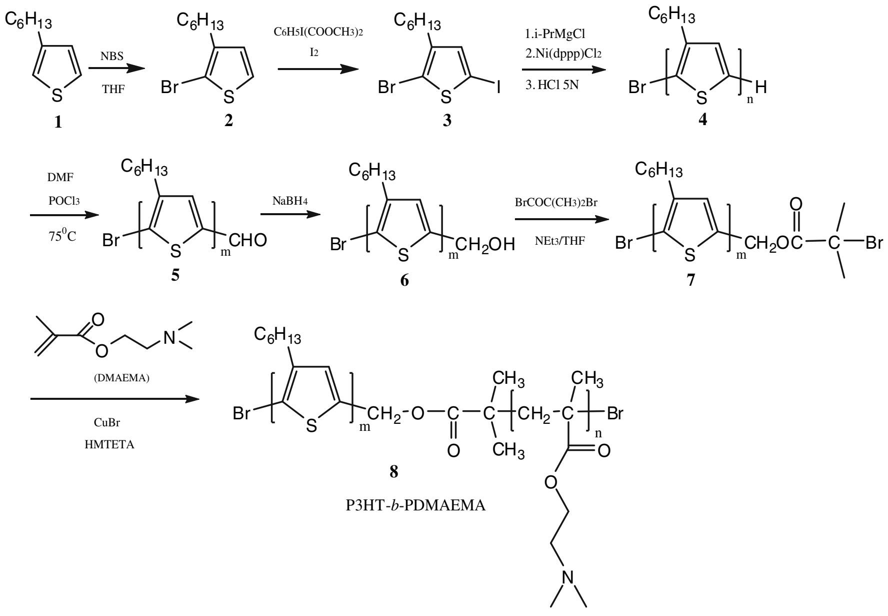
The polymerization was performed in anhydrous THF by using P3HT-Br, CuBr, HMTETA as macroinitiator, catalyst, and ligand, respectively. The initial molar ratio was $[M]_0$:$[P3HT\text{-}MI]_0$:$[CuBr]_0$:$[HMTETA]_0$ = 50:1:1:2. A dry flask was charged with CuBr (3.37 mg, 0.023 mmol), HMTETA (12.7 μL, 0.046 mmol), THF (0.6 mL), and a magnetic stirrer. The flask was fitted with a rubber septum and degassed with three successive vacuum nitrogen cycles. A second flask was charged with the P3HT-macroinitiator (150 mg), DMAEMA monomer (197.5 μL 1.17 mmol), and THF (2 mL). The flask was fitted with a rubber septum and degassed under nitrogen flow for a few minutes. The mixture was then transferred into the first flask and the polymerization was carried out under stirring at 60 °C for 16 h. The reaction was stopped by cooling down the reaction medium in liquid nitrogen. Then, THF was added to dilute the solution. Copper catalyst was removed by filtration of the THF solution through an alumina oxide column. The diblock copolymers were recovered by precipitation from cold heptane, filtration and drying up to constant weight. ^1H NMR (300 MHz, $CDCl_3$); δ (ppm): 6.96 (s, 1H), 5.29 (s, 2H), 4.06 (s, 2H), 2.78 (t, 2H), 2.57 (s, 2H), 2.28 (s, 6H), 1.90 (s, 2H), 1.69 (sex, 2H), 1.49 (q, 6H), 1.04 (s, 9H), 0.89 (t, 3H). GPC, 12,960 g/mol. PDI, 1.37.

Characterizations

^1H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with TMS as an internal reference, on a Bruker AMX-300 spectrometer at a frequency of 300 MHz. Fourier transform infrared (FT-IR) spectra were recorded using a BIO-RAD Excalibur spectrometer equipped with an ATR Harrick Split PeaTM. Size exclusion chromatography (SEC) of P3HT was performed in THF (sample concentration: 1 wt%) at 35 °C using a polymer laboratories (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 mL/min), a Basic-Marathon Autosampler, a PL-RI refractive index detector and three columns: a guard column PL gel 10 μm and two columns PL gel mixed-B 10 μm. Molecular weight and molecular weight distribution were calculated with reference to polystyrene standards. MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10,000. All the samples were analyzed using *trans*-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB), that matrix was prepared as 20 mg/mL solution in CH_2Cl_2. The matrix solution (1 μL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH_2Cl_2 to obtain 1 mg/mL solutions. 1 μL aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 750 to 3000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. UV–vis absorption spectra of a polymer solution in the solvents and a thin film were recorded on a Cary UV–vis 50 Varian spectrometer over a wavelength range of 400–700 nm. Modulated differential scanning calorimetry (MDSC) measurements were carried out with a MDSC Q2920 apparatus from T.A. Instruments under nitrogen flow (heating rate 3 °C/min). The contact angle measurements were performed using a Drop Shape Analysis System DSA 10 Mk2 (Krüss) equipped with a thermostated chamber and a Circulator Thermo HAAKE DC 10.

Results and discussion

Poly(3-hexylthiophene)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (P3HT-*b*-PDMAEMA) block copolymers (Scheme 1) were synthesized using a five-step procedure consisting first of a controlled ‘quasi-living’ Grignard metathesis (GRIM) polymerization of 2-bromo-5-iodo-3-hexyl thiophene monomers in presence of $Ni(dppp)Cl_2$ to form α-bromo, poly(3-hexyl thiophene) (Br-P3HT-H). Then, the quantitative conversion of Br-P3HT-H into α-bromo, ω-bromoisobutyrate poly(3-hexyl thiophene) (**7**) was performed by a three-step procedure, finally followed by ATRP of DMAEMA monomer as initiated by the macroinitiator **7**. As far as the GRIM polymerization is concerned, treatment of 2-bromo-5-iodo-3-hexyl thiophene (**3**) with 1 equiv of iPr-MgCl results in magnesium-iodine exchange reaction, also referred to a Grignard metathesis (GRIM) reaction. Then, the “activated monomer” has been polymerized in presence of $Ni(dppp)Cl_2$ for an initial monomer-to-nickel molar ratio of 73 (molecular weight at 100% conversion is 10,400 g/mol). The polymerization has been performed in THF at 0 °C for 24 h and quickly terminated by addition of a 5 M HCl solution to prevent any transhalogenation side-reaction. As determined by gravimetry, a conversion of 70% has been recorded $\left(\overline{M}_{\mathrm{nth}} = 7280\ \mathrm{g/mol}\right)$. A good correlation between the theoretical molecular



Scheme 1 Synthesis of poly(3-hexylthiophene)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (P3HT-*b*-PDMAEMA) diblock copolymers

weight $\left(\overline{M}_{\mathrm{nth}}\right)$ and the value determined by gel permeation chromatography (GPC) ($M_{\mathrm{n\ exp}} = 6000$ g/mol) is obtained attesting for the control over the GRIM polymerization, which is further confirmed by the symmetrical and narrow molecular weight distribution characterized by a low polydispersity index (PDI = 1.18). A high regioregularity content (>99%) was determined by ^{1}H NMR while the presence of the expected end-groups (H/Br) was fully evidenced by MALDI-ToF analysis (see S1, Supporting info).

A formyl-de-hydrogenation of the as-obtained α-bromo P3HT (Br-P3HT-H) protic end-group was successfully performed by Vilsmeier reaction (second step). The evolution of the reaction was followed by MALDI-ToF analysis until complete transformation of the α-bromo P3HT (**4**) to α-bromo, ω-fornyl P3HT (**6**) (data not show here). After completion of reaction (24 h at 75 °C), the formyl end group was reduced by $NaBH_4$ yielding the expected P3HT-OH (**6**) in the third step of the synthetic procedure.

The fourth step consisted of quantitative conversion of P3HT-OH into ATRP macroinitiator via esterification reaction of the terminal hydroxyl group with α-bromoisobutyryl bromide in the presence of triethylamine. The reaction was performed in THF at 50 °C for 12 h and P3HT-Br macroinitiator (**7**) was recovered by selective precipitation from cold methanol.

In addition to the appearance of the carbonyl vibrational signal (υ C=O) observed by FT-IR at 1733 cm^{-1}, the effectiveness of the esterification step has been highlighted by ^{1}H NMR analysis. ^{1}H NMR spectrum (Fig. 1, bottom) displays the complete disappearance of the initial α-hydroxy methylene protons present at

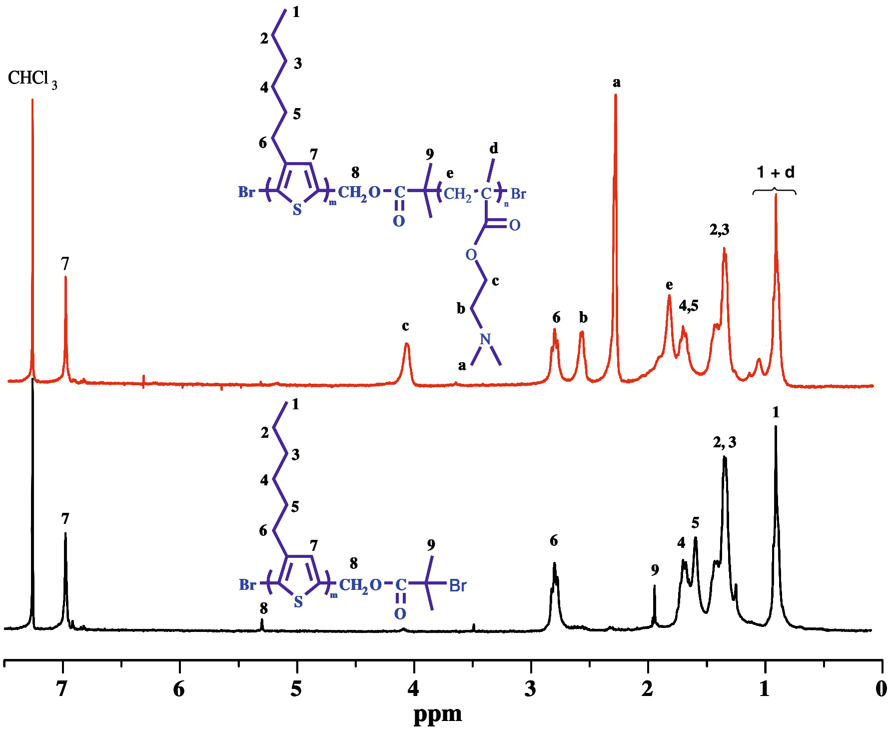


Fig. 1 ^{1}H-NMR spectra recorded in $CDCl_3$ of P3HT-Br (*bottom*) and the associated P3HT-*b*-PDMAEMA (entry 1, Table 1) (*top*)

4.7 ppm, while new signals corresponding to the oxycarbonyl methylene protons (H_8) and to the methyl protons of the α-bromoisobutyrate end-group (H_9) are detected at 5.3 and 1.9 ppm, respectively, attesting for the quantitative esterification of the terminal hydroxyl groups. $\overline{M}_n$ of P3HT-Br chains reaches about 6400 g/mol as determined by ^{1}H NMR from the relative intensity of methylene repetitive groups (H_6) and the methyl groups from the end-group residue. In very good correlation, an $\overline{M}_n$ of 6900 g/mol has been determined by GPC while the PDI remains narrow (1.23).

Finally the synthesis of poly(3-hexylthiophene)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (P3HT-*b*-PDMAEMA) block copolymers has been performed by ATRP of *N*,*N* dimethylamino-2-ethyl methacrylate (DMAEMA) at various temperatures and for different PDMAEMA block lengths by using P3HT-Br (**7**) as the macroinitiator ([DMAEMA]/[P3HT-Br]/[CuBr]/[HMTETA] = 25/1/1/2, 50/1/1/2, and 75/1/1/2). The polymerizations were performed in THF for 16 h in presence of a CuBr/HMTETA catalytic system under dry nitrogen atmosphere. The polymerizations were stopped by cooling of the reaction mixture followed by dilution with an extra volume of THF. Copolymers were recovered by precipitation from cold heptane.

The polymerization degree of PDMAEMA block was calculated from the recorded ^{1}H NMR spectra by comparing the relative intensities of the α-amino methylene protons of DMAEMA residue from repeating unit at $\delta = 2.3$ ppm (H_a) and the methine (ring) proton of P3HT at $\delta = 6.96$ ppm (H_7) taking into account the $\overline{M}_n$ of macroinitiator (P3HT-Br, Fig. 1). It is worth pointing out that to optimize the synthetic conditions of P3HT-*b*-PDMAEMA block copolymers, two temperatures of reaction were investigated for the ATRP reaction keeping all other parameters unchanged. As seen from Table 1, relatively high PDMAEMA conversions were obtained and good accordance between theoretical and experimental molar masses $\left(\overline{M}_{n\,exp}\right)$ attesting for an initiation efficiency close to 1 whatever the temperature and the targeted compositions. Thus, the polymerization of DMAEMA initiated by P3HT-Br (**7**) was also performed in a controlled manner. An additional evidence for the controlled synthesis of the copolymers is the symmetrical and narrow molecular weight distribution recorded by SEC. PDI values of the block copolymers are comprised between 1.3 and 1.4 (Table 1) for overall molecular weights going from 8300 to 16,600 g/mol. Figure 2 clearly shows the shift to higher elution volumes of a representative diblock copolymers (Table 1, entry 2) compared to the trace initially recorded for the P3HT-Br macroinitiator.

Depending on the relative content in poly(*N*,*N*-dimethylamino-2-ethyl methacrylate), the diblock copolymers are expected to be soluble in a wider range of solvents than in case of the conjugated P3HT. UV–vis spectroscopy can be used to probe the π overlap of conjugated polymers both in solution and in solid-state film. Table 2 presents the solution (in various solvents) and solid state UV–vis spectra results recorded for both regioregular P3HT ($M_n = 6400$ g/mol; PDI = 1.23) and a

Table 1 Macromolecular characteristic features of P3HT-*b*-PDMAEMA as obtained from P3HT-Br ($\overline{M}_{n\,exp} =$ 6,400, PDI = 1.23) by DMAEMA ATRP process using a Cu/HMTETA ([CuBr]/[HMTETA] = 1/2) catalytic complex

Copolymer	[DMAEMA]/[P3HT-Br]	T (°C)	Conv.[a]	PDMAEMA			P3HT-*b*-PDMAEMA	
				$\overline{M}_{nth}$[b]	$\overline{M}_{n\,exp}$[c]	f[d]	$\overline{M}_{n\,NMR}$	$\overline{M}_w/\overline{M}_n$[e]
1	25	60	48	1,880	1,900	0.99	8,300	1.29
2	50	60	78	6,120	6,560	0.93	12,960	1.37
3	50	80	80	6,280	6,750	0.93	13,150	1.37
4	75	60	83	9,700	10,200	0.95	16,600	1.30

[a] Conversion as determined after precipitation from cold heptane: Conv. = $(m - m_I - m_{Cu} - m_L)/m_M$ where m denotes the weight of product, and m_I, m_{Cu}, m_L, m_M the weights of the initiator, copper catalyst, ligand (HMTETA), and monomer, respectively

[b] PDMAEMA theoretical number–average molar mass as calculated by $[\text{DMAEMA}]_0/[\text{P3HT-Br}]_0 \times \text{Conv} \times M_w$ DMAEMA assuming a living/controlled process

[c] PDMAEMA experimental number–average molar mass as determined by ^{1}H NMR spectroscopy (see Fig. 1): $\overline{M}_{n\,exp} = DP_{exp}\ x\ M_w$DMAEMA, where DP_{exp} is the experimental degree of polymerization, as calculated from the relative intensities of methylene protons of DMAEMA ($\delta = 2.58$ ppm) and of the methine protons of P3HT units ($\delta = 6.96$ ppm)

[d] Initiation efficiency factor as calculated from $\overline{M}_{nth}/\overline{M}_{n\,exp}$

[e] Polydispersity index as determined by GPC in THF at 35 °C

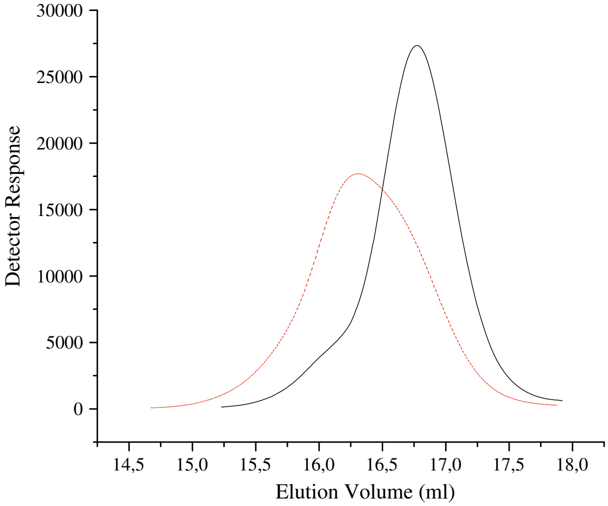


Fig. 2 GPC traces of P3HT-Br macroinitiator (*straight line*) and the associated P3HT-*b*-PDMAEMA (*dotted line*) (Table 1, entry 2)

representative P3HT-*b*-PDMAEMA (Table 1, entry 2). In non (or poorly) polar solvents such as THF, chloroform, toluene, both P3HT, and P3HT-*b*-PDMAMEMA show very similar single maximum absorption (λ_{max}) for the π–π^* transition at around 445 nm (see S2, supporting info). However, in more polar solvents such as ethanol and water, two or three absorption peaks are observed.

In water as well as for a solid-state film, the λ_{max} values of the two polymers are bathochromically shifted to around 554 nm. Both P3HT and P3HT-*b*-PDMAEMA also revealed a shoulder at around 606 nm related to vibronic absorption, indicating

Table 2 UV–vis absorption peaks for regioregular P3HT and P3HT-*b*-PDMAEMA recorded in solution or on solid-state films

Solvent	P3HT-*b*-PDMAEMA (λ = nm)	P3HT (λ = nm)
Chloroform ($CHCl_3$)	455	452
Tetrahydrofuran (THF)	443	447
Toluene	445	451
Acetonitrile	505, 553	Insoluble
Acetone	490	Insoluble
1,4-Dioxane	450	Insoluble
Carbon tetrachloride (CCl_4)	434	438
Ethanol	505, 553	Insoluble
Ethyl acetate	430	Insoluble
Heptane	Insoluble	Insoluble
Cyclohexane	Insoluble	Insoluble
Water (pH: 5.8)	500, 552, 590	Insoluble
Solid-state film	524, 554, 606	527, 558, 602

a high degree of ordering in the polymer films even when amorphous PDMAEMA is covalently linked to P3HT [27]. These results propose that the flexible coil PDMAEMA chains do not perturb to a large extent the long range order of rod-like P3HT chains, maintaining good optical properties.

As highlighted by Table 2, P3HT-*b*-PDMAEMA is highly soluble in a large variety of solvents including water. PDMAEMA homopolymer is a water-soluble and pH-sensitive polymer, cationic when protonated, and characterized by a p*K*a value at around 7.5 [28, 29]. Being of same interest than the grafted structures reported by Winnik (see "Introduction" section) [26], we have been also interested in investigating the effect of pH of the water solution on the optical properties of the P3HT block.

Figure 3 shows the absorption of P3HT-*b*-PDMAEMA in water at different pH values. When increasing pH higher than 8, P3HT-*b*-PDMAMEA gets insoluble in water. Hence, at this alkaline pH values, there is no longer absorption peak. Upon decreasing pH from 7 to 2, the previously precipitated diblock becomes soluble (Fig. 4) and a peak at 520 nm and two shoulders at 552 and 605 nm are observed.

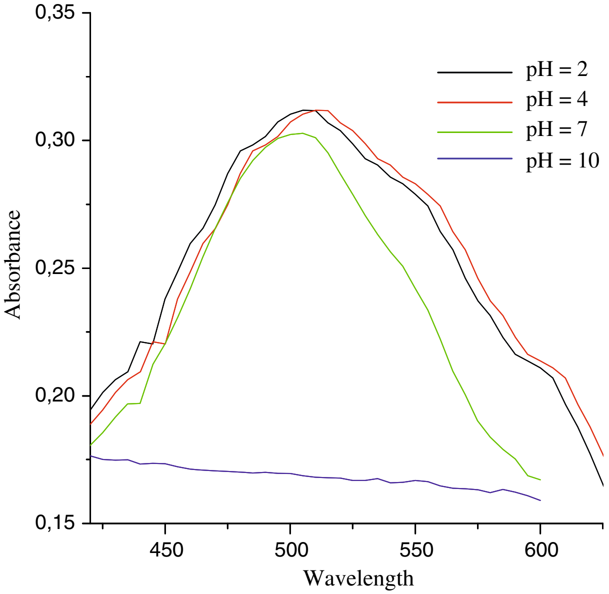


Fig. 3 UV–vis absorption spectra of P3HT-*b*-PDMAEMA in water at different pH values

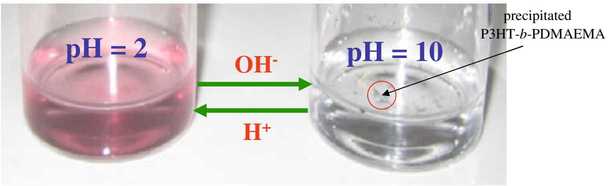


Fig. 4 The color exchange of P3HT-*b*-PDMAEMA in pH 2 and pH 10

The pH dependence of the solubility of P3HT-*b*-PDMAEMA diblock copolymers can be attributed to the different solubility of PDMAEMA at various pH. Water is a non-solvent of the poly(3-hexylthiophene) block, whereas PDMAEMA is strongly protonated at acidic pH. In acidic conditions (pH 2), protonation of the dimethylamino groups makes the PDMAEMA chains positively charged. The solubility and repulsion of the positively charged PDMAEMA block are stronger and tend to dissociate the bridging existing between the P3HT-*b*-PDMAEMA molecules and at the same time, stretch the P3HT backbone. As a consequence, the P3HT backbone is less folded and twisted at pH 2 than at pH 10, resulting in an increase of the average conjugation length and an appearance of absorption peaks.

Thermal properties of both P3HT (M_n = 6400 g/mol; PDI = 1.18) and a representative P3HT-*b*-PDMAEMA (Table 1, entry 2) were investigated by modulated differential scanning calorimetry (MDSC). MDSCs of homo P3HT and P3HT-*b*-PDMAEMA are shown in Fig. 5. For such studied molecular weight, the glass transition temperature (T_g) value of PDMAEMA is around 38 °C. On the other hand, the melting point (T_m) of a 6400 g/mol P3HT is observed at ca. 192 °C [30]. P3HT-*b*-PDMAEMA diblock copolymers exhibit both a T_g at ca. 38 °C and a T_m at ca. 193 °C, which correspond to the PDMAEMA and P3HT segments, respectively. This result supports again the phase segregation occurring in the P3HT-*b*-PDMAEMA block copolymers.

Having in mind that the presence of an ionogenic PDMAEMA block can impart hydrophilicity to the P3HT-based materials, experiments for determination of the water contact angle at the surface of P3HT, and P3HT-*b*-PDMAEMA was performed as well. While the contact angle value of a regioregular P3HT film is 105° (±1°), the value determined for a P3HT-*b*-PDMAEMA (Table 1, entry 4) drops down to 77° (±1°). This result clearly highlights the key-effect displayed by the introduction/anchoring of PDMAEMA sequences into P3HT to the surface wettability of the diblock copolymer materials. This is of special interest in terms of

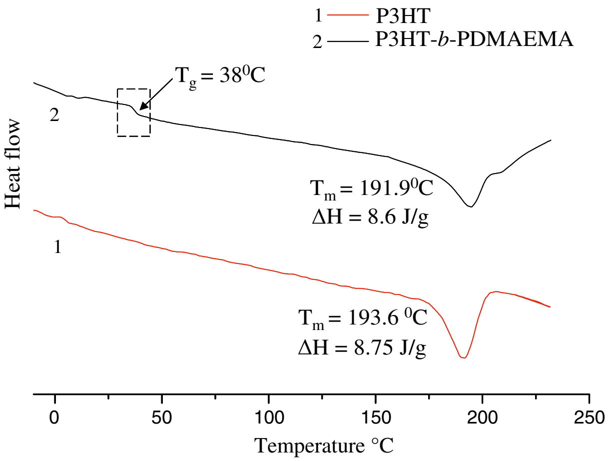


Fig. 5 MTDSC thermograms of (*1*) homo P3HT and (*2*) P3HT-*b*-PDMAEMA (Table 1, entry 2)

printing process for the fabrication of transistors based on P3HT and poly(styrene-sulfonic acid) (PSSH) [31, 32] as it will be reported in a forthcoming paper.

Conclusions

Perfectly controlled poly(3-hexylthiophene)-block-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) diblock copolymers (P3HT-*b*-PDMAEMA) were synthesized by a combination of 'living' GRIM, end-group modification and ATRP reaction. The resulting diblock copolymers were characterized by using ^{1}H NMR, GPC, FT-IR, UV–vis spectroscopy and MDSC as well as measurement of contact angles recorded on films produced by solvent-casting. The copolymers exhibit the behavior typical for an amphiphilic diblock copolymers and was found to be readily soluble both in a large variety of organic solvents and in acidic water ($\mathrm{pH} \leq 7$) permitting the correlation between the conformation states and the optical properties of the regioregular rrP3HT chains in solution with the polarity of the solvent. UV–vis spectra revealed the presence of a vibronic structure in most polar solvents, pointing to the long range ordering of rrP3HT caused by the self assembly of an amphiphilic P3HT-*b*-PDMAEMA in these solvents. MDSC results evidenced clearly the phase segregation of each domain of the P3HT-*b*-PDMAEMA copolymers. Finally, it is worth pointing out that the introduction of PDMAEMA into P3HT-*b*-PDMAEMA diblock copolymers allows for significantly improving the surface wettability of high interest in fabrication of electronic devices.

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