

Polystyrene functionalized with EDOT oligomers

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Received 14 August 2007; received in revised form 18 November 2007; accepted 3 December 2007
Available online 18 January 2008

Abstract

The control of the organization of polymeric films from the nano- to the meso-scale is an ongoing field and different approaches have been proposed by many authors with the aim to drive the organization and the morphology of the materials to optimize their properties. One of the driving force of the organization at the micrometric and submicrometric scale is the degree of interaction between different polymeric chains and many successful examples of ordered supramolecular organization based on nano and microphase separation have been reported by using block copolymers and polymer blends. In this work we report on a synthetic approach to prepare a copolymeric structure formed by polystyrene and 3,4-ethylenedioxythiophene (EDOT) oligomers with the aim of preparing thin polymeric films exhibiting organized morphologies.

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Keywords: Copolymer; Polystyrene; EDOT; Selforganized structures

1. Introduction

The development of conjugated polymers suitable for optoelectronic applications has led to synthesize new unconventional structures with the aim of finding functional materials exhibiting not only improved electrooptical properties, but also other functionalities such as selforganization in desired structures or morphologies suitable for specific applications in devices. To reach this goal a careful

planning and choice of the main conjugated backbone, of the functional groups necessary to solubilize the structures and of the number and kind of polar–apolar groups in the backbone, has to be followed. All these factors are extremely important in establishing the final organization of the materials which will be used as active materials in different devices with the aim of improving their performances. It is worthwhile to note that the level of organization ranging from the nano- to the mesoscopic scale can be further improved if block copolymeric structures leading to ordered nanophase separation are considered. An example of this smart approach is reported in Ref. [1] where a triblock copolymer, containing thiophene oligomers

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as side chains, has been used to prepare a regular selfassembled structure, hierarchically organized. Similar results, providing ordered phase separation at the micrometric scale, have been shown by Han et al. [2] in a blend of two nonconjugated polymers, poly(2-vinylpyridine) and polystyrene (PS), and in conjugated systems such as a blend of poly(9,9-dioctylfluorene) and poly(9,9-dioctylfluorene-alt-benzothiadiazole) [3].

In this work we have synthesized block copolymers containing EDOT oligomers as side chains with the aim of obtaining ordered morphologies as a result of the structure of the copolymer.

2. Experimental

2.1. General

Tetrahydrofuran (THF) and toluene (Riedel de Haën) was used after distillation under nitrogen, from K/benzophenone and Na/K alloy, respectively. UV-vis and PL spectra were performed in chloroform (Puriss, PA, Riedel de Haën) solution with concentration of 0.1% by weight.

2-Isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane was the Aldrich product; EDOT was supported by Bayer and used after distillation. Butyl-lithium solution 1.6 M was supported by Fluka. Styrene (Aldrich) was distilled prior to use under reduced pressure in N₂ after stirring with CaH₂ at 40–50 °C for 30 min.

The synthetic pathway followed to prepare the monomer and the polymeric and copolymeric structures is reported in Scheme 1.

Thin films exhibiting the periodic holes on the surface have been prepared as described in Ref. [4]. Films were deposited onto microscope cover glasses previously cleaned with acetone and chloroform and dried in an oven at 70 °C.

UV-vis spectra were recorded on a Perkin-Elmer Lambda 900 Spectrometer and PL measurements were obtained with monochromator equipped with a CCD detector, by exciting with a monochromated Xenon lamp.

AFM measurements were carried out with an NTEGRA Probe NanoLaboratory from NT-MDT, operated under atmospheric conditions and equipped with a standard cantilever for semicontact mode (NT-MDT, resonant frequency 230 kHz).

¹H NMR spectra were recorded with a 400 MHz Bruker Avance Instrument at RT.

2.2. Preparation of 4,4',5,5'-tetramethyl-1,3,2-dioxaboronic ester of EDOT (2)

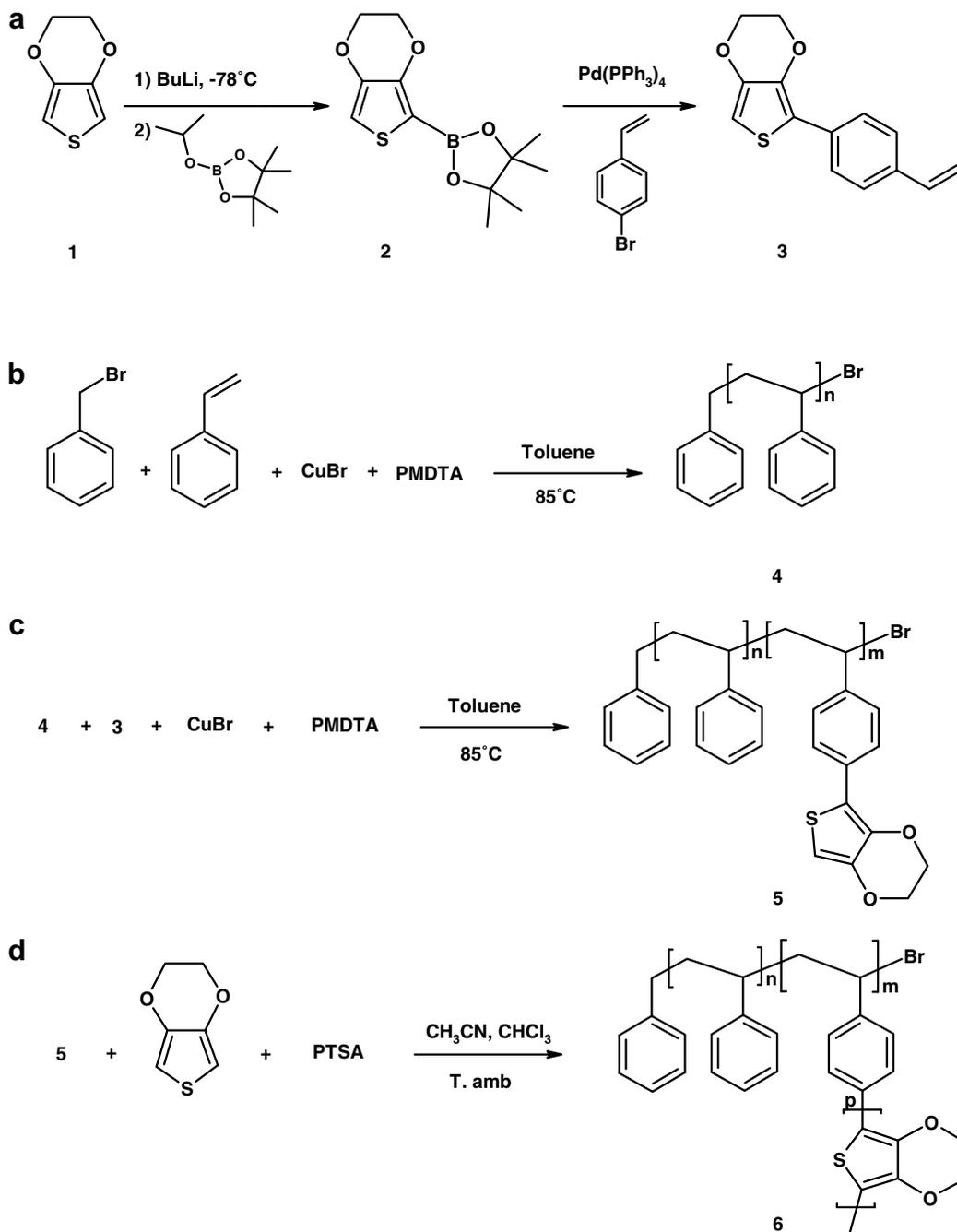
A solution of 3,4-ethylenedioxythiophene (2 g, 14.1 mmol) in dry THF (30 ml) was cooled to –78 °C under N₂ and 10.4 ml of *n*-BuLi solution (1.5 M, 15.5 mmol) was slowly added. The mixture was stirred at 0 °C for 20 min and then recooled to –78 °C. At this temperature the reaction was treated with 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (8 ml, 39 mmol), and the mixture was stirred for 6 h. The reaction was poured into crushed ice/NH₄Cl and the product was then extracted with Et₂O (3 × 30 ml). After drying over MgSO₄ the solvent was removed at reduced pressure. The white solid product was used without further purification with purity GC = 88.2% (2.62 g, 61%). ¹H NMR (CDCl₃) δ 6.56 (s, 1H), 4.25–4.22 (m, 2H), 4.12–4.09 (m, 2H), 1.26 (s, 12H).

2.3. *p*-EDOTStyrene (EDsty) (3)

A nitrogen-flushed three-neck round bottom flask was charged with boronic ester of EDOT (2) (2 g, 7.44 mmol), bromo styrene (1.24 g, 6.76 mmol), Pd(PPh₃)₄ (390 mg, 0.34 mmol), dry THF (60 ml) and 2 M degassed solution of K₂CO₃ (30 ml). After refluxing overnight the reaction mixture was quenched with water, extracted three times with ether and dried over MgSO₄. The solvent was removed at reduced pressure and the mixture was purified by flash chromatography using silica gel and hexane/ethyl acetate 9:1 as eluent. A second column with reverse phase silica and methanol as eluents was necessary to remove the trace of EDOT still present, to afford 3 as a yellow oil (730 mg, 44%). ¹H NMR (CDCl₃) δ 7.56 (d, 2H, *J* = 8.3 Hz), 7.32 (d, 2H, *J* = 8.6 Hz), 6.68–6.58 (dd, 1H, *J*_{trans} = 17.6 Hz and *J*_{cis} = 10.8 Hz), 6.22 (s, 1H), 5.67 (d, 1H, *J* = 17.6 Hz), 5.16 (d, 1H, *J* = 10.8 Hz), 4.25–4.22 (m, 2H), 4.18–4.15 (m, 2H). UV (CHCl₃) λ_{max} = 322 nm.

2.4. Polystyrene-Br terminated (4)

Into a dry schlenk flask equipped with a stir bar CuBr (168 mg, 1.17 mmol), PMDTA (405 mg, 2.34 mmol) and dry toluene (10 ml) were added. The mixture was deoxygenated by fluxing nitrogen for 30 min. Styrene, previously deoxygenated (3 g, 29.6 mmol), and benzyl bromide (100 mg,



Scheme 1.

0.59 mmol) were introduced into the schlenk and frozen in liquid nitrogen. After three freeze/pump/thaw cycles, the schlenk was placed in an 85 °C oil bath and stirred overnight. After polymerization was complete, the reaction mixture was stirred in air for 20 min to allow the oxidation of Cu(I) to

Cu(II). PS was recovered as a white solid by precipitation in methanol, 1.03 g (33.2%). GPC (THF) $M_n = 10335$, $M_w = 11931$, $DPI = 1.1$. ^1H NMR (CDCl_3) all signals are broad: δ 7.13, 7.08, 6.62 and 6.51 are phenyl protons, 1.88 ($-\text{CH}-\text{CH}_2-$), 1.47 ($-\text{CH}-\text{CH}_2-$).

2.5. Preparation of block copolymer PS-*b*-PSEDOT (5)

The macroinitiator **4** (216 mg, 0.016 mmol), EDSty **3** (400 mg, 1.6 mmol), CuBr (23.4 mg, 0.16 mmol) and PMDTA (56.5 mg, 0.326 mmol) were added to a dry schlenk flask. Toluene (10 ml), previously deoxygenated, was added to the reaction. The mixture was frozen in liquid nitrogen and after three freeze/pump/thaw cycles, the schlenk was placed in an 85 °C oil bath and stirred overnight. The polymer was precipitated three times in methanol and dried under high vacuum. ¹H NMR (CDCl₃) all signals are broad: δ 7.09, 7.04, 6.57 and 6.47 are phenyl protons, 6.24 (H in α position of EDOT), 4.19 (–OCH₂CH₂O–), 1.84 (–CH–CH₂–), 1.42 (–CH–CH₂–). UV (CHCl₃) λ_{max} = 298 nm. The number of EDOT rings was evaluated by comparing the intensities of the aliphatic hydrogen of the EDOT units with the intensities of the aromatic protons. An average number of 4 EDOT rings/polystyrene chain was evaluated with the reaction condition above reported.

2.6. Side chain extension with EDOT

Distilled EDOT (0.6 ml) was dissolved in 80 ml of a mixture of acetonitrile and chloroform (5/3). To this solution 900 mg of *p*-toluensulfonic acid was added stepwise. After 2 days of reaction a solution of 45 mg of **5** in 4 ml of chloroform was added. The mixture was left under magnetic stirring for 48 h at RT. The solution was then reduced in volume to 5 ml and was twice precipitated in methanol.

The resulting powder was dissolved in chloroform, filtered and again precipitated in methanol. The resulting powder was extracted with acetone to avoid the presence of EDOT oligomers.

The ¹H NMR of the copolymer obtained does not differ from copolymer **5**, the only difference being the increased intensity of the 4.19 ppm peak attributed to the bridge protons (–OCH₂CH₂O–) of EDOT. According to this increase the number of EDOT rings/polystyrene chain is about 10.

3. Results and discussion

The use of atom transfer radical polymerization (ATRP) has allowed to synthesize copolymeric structures with a good control of the molecular weight and of their distribution [5]. Moreover initiation of an ATRP polymerization with brominated

benzylic groups has opened new possibilities in the formation of block copolymers [6] without the presence of carbonyl groups in the initiator molecule, which can be undesired because of the reactivity of the carbonyl groups. For this reason we have started the formation of the styrene block (**4**) with benzyl bromide as shown in Scheme 1b. The resulting polymers exhibited narrow distribution of molecular weight, $M_w/M_n = 1.1$, indicating a living character and M_n of 10335.

In the subsequent step the substituted monomer (EDSty, **3**) was introduced to form the second block of the copolymer. The EDSty unit, exhibiting an absorption spectrum centered at 322 nm in THF, was prepared according to Scheme 1a through a Suzuki coupling. The macroinitiator (**4**) was used to start polymerization of monomer **3** with the same procedure used for the preparation of polymer **4** obtaining copolymer **5** (Scheme 1c). A small, but significant increase of M_n (10601) was found in copolymer **5** with respect to the starting macroinitiator indicating that one/two monomeric units of **3** were introduced for each polystyrene macroinitiator chain.

The structure of copolymer **5**, as detected by ¹H NMR, resulted to be formed, on the average, by a block of 100 styrene units connected to a second short block of 4 EDSty units linked together. According to ¹H NMR analysis the increase in molecular weight due to EDSty units should be the double of the value as detected by GPC. It is worthwhile to mention that GPC measurements on copolymer **5** cannot give a real determination of its molecular weight. In fact the addition of EdSty units changes the structure of the polymer backbone because of the presence of the EDOT units, so that a direct relationship with the polystyrene standard samples used for preparation of the calibration curve is not completely correct. For this reason we believe that the data obtained from NMR analysis can give a real value of the ratio between monomer **3** and styrene units.

The presence of EDSty units was confirmed by the UV–vis spectrum showing the absorption band of EDOT peaked at 300 nm in chloroform solution (Fig. 1a). This absorption is centred at higher energy with respect to the EDSty monomer (λ_{max} = 322 nm): in fact, during the radical polymerization process the vinyl bond reacts so that the conjugation length of the EDSty unit is lowered.

To prepare the diblock copolymer, **5** was subsequently used as “capping group” in an EDOT

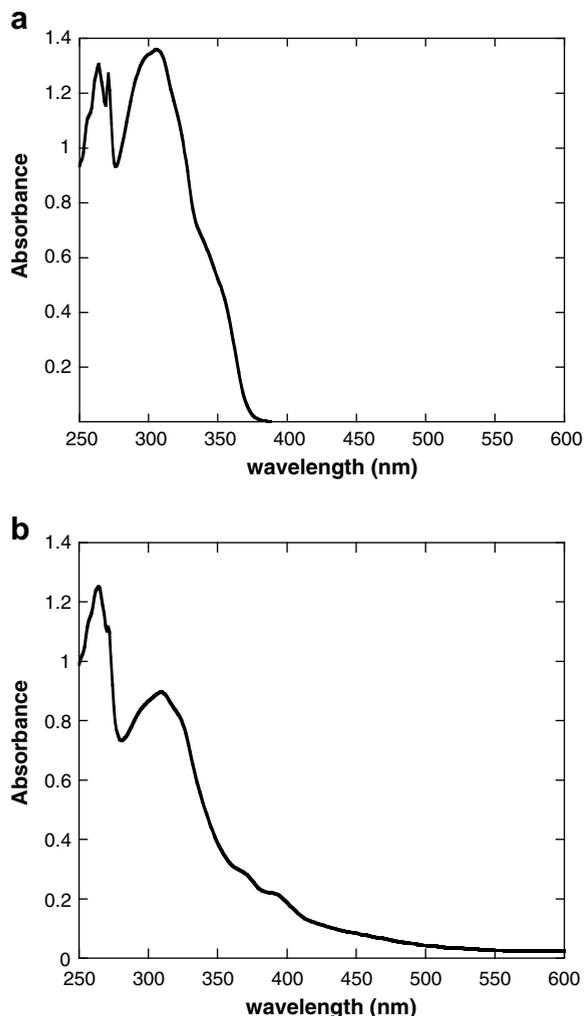


Fig. 1. (a) Absorption spectrum of copolymer **5**: the peak at 255 nm has been attributed to the absorption of polystyrene. (b) Absorption spectrum of copolymer **6**.

polymerization performed in acetonitrile in the presence of *p*-toluenesulfonic acid. This approach was successfully introduced by Scherf and co-workers [7] for the preparation of polyfluorene/polyaniline block copolymers. In that case brominated polyaniline was used as an end capper in the polymerization of dialkylsubstituted fluorene by means of Suzuki coupling. The polyaniline homopolymer, which is insoluble, was removed by extraction of the soluble copolymer by a proper solvent.

In our case we started the polymerization of EDOT in acetonitrile/chloroform mixture by means of *p*-toluenesulfonic acid (PTSA). During EDOT homopolymerization, copolymer **5** was introduced in the EDOT solution as described in the experi-

mental section. After the reaction, precipitation of the polymer in an excess of methanol was performed and the polymeric powder was repeatedly extracted with acetone to extract the soluble copolymeric structure. The part which was soluble in acetone, copolymer **6**, was characterized by GPC giving $M_n = 11.900$, $M_w = 16.690$ and an increased polydispersity (1.4) with respect to the starting copolymer **5**. We believe that this increase in molecular weight, as previously discussed, cannot give a true indication of the number of EDOT units linked to the copolymer because the addition of EDOT units to the copolymeric structure changes the copolymer composition. However the detected change in the molecular weight and of its distribution is a clear indication that the structure of the copolymer has been modified due to the addition of EDOT units.

Copolymer **6** was investigated also by UV–vis spectroscopy in solution. In Fig. 1b its spectrum is reported, exhibiting an absorption maximum centred at 310 nm with a tail and low intensity peaks to 420 nm. This value indicates that the conjugation length of the PEDOT chain is rather short being related to the conjugation path of a dimer/trimer rather than to a conjugation length of a polymeric EDOT. The above reported absorption peaks are in agreement with the data by Roncalli and co-workers [8] for soluble EDOT oligomers end-capped with hexyl chains: dimers, trimers and tetramers show a structured absorption with the main peak centred at 330, 390 and 430 nm, respectively.

The structure of copolymer **6** was further investigated by means of ^1H NMR: we compared the intensities of the aliphatic protons of EDOT with the intensities of the aromatic proton of the polystyrene backbone obtaining an increased ratio of the EDOT/styrene with respect to copolymer **5**. This value indicates that, on the average, 10 EDOT monomers are linked to the copolymer backbone.

As above mentioned copolymer **5** structure is formed by two different blocks with different lengths: a long sequence of styrene units connected to four EDSty units linked together. During polymerization, as shown in Scheme 1d, some new EDOT units have been linked to the EDOT units already present on the main backbone. In Fig. 2, a schematic picture of copolymer **6** structure in agreement with the experimental data is reported.

The presence of different lengths of EDOT units in the backbone has been evidenced by studying the behaviour of the photoluminescence of **6** at different wavelengths.

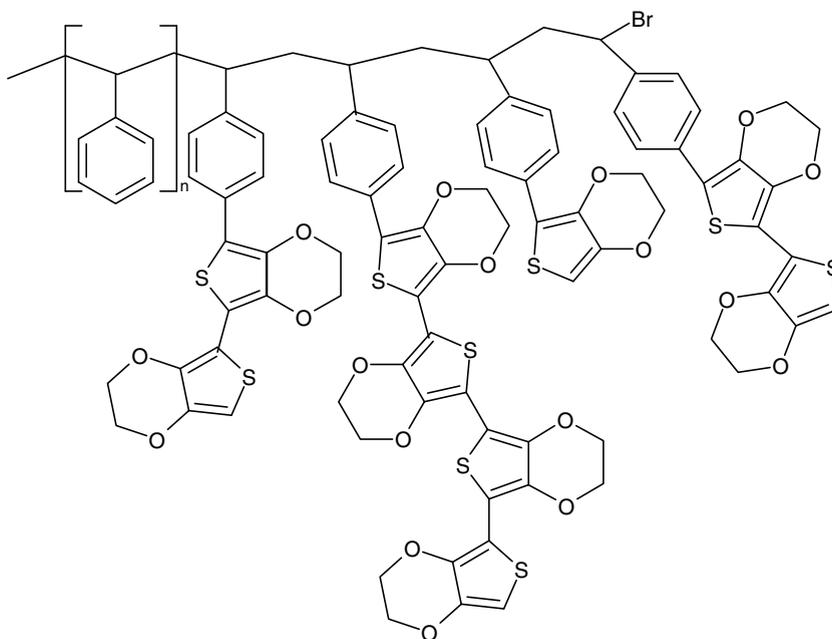


Fig. 2. The structure of copolymer 6.

As shown in Fig. 3, by changing the excitation wavelength of dilute solutions of copolymer 6, the shape and position of the PL peaks change.

With an excitation at 300 nm only a peak at 400 nm with a long tail of 550–600 nm in the emission has been detected and attributed to the feeble emission from EDOT. By increasing the excitation wavelength to 380 nm two different peaks appear

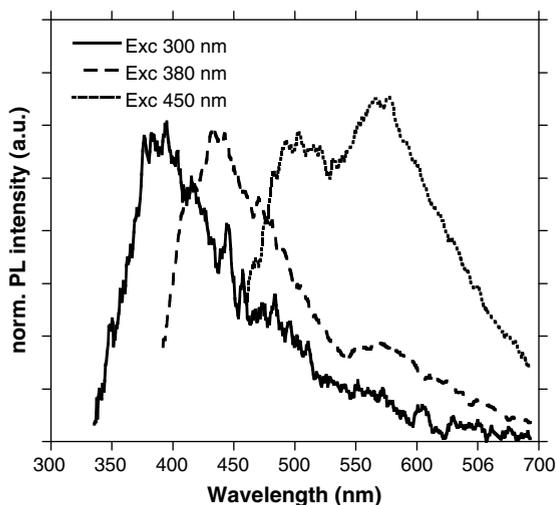


Fig. 3. Photoluminescence spectra of copolymer 6 solution at different excitation wavelengths.

at 440 and 570 nm, while by exciting at 450 nm two emission peaks appear at 500 and 570 nm. These data can be explained by assuming that different emitting species, attributed to EDOT sequences with different conjugation lengths, are present in the copolymer solution and that energy transfer processes among them might happen. To have energy transfer processes in dilute solution among different emitting species their reciprocal distance should be lower than 20 nm and this occurs only if these species are linked to the same backbone. These findings further support the structure of the copolymer as shown in Fig. 2.

Attempts to increase the length of EDOT units linked to the main backbone are under investigation.

3.1. Formation of patterned structures

In a previous work [4] we have shown that polystyrene solutions after evaporation in given conditions, can form thin films with a particular structure, i.e. the surface of the film is covered by a regular array of holes connected to cavities which are localized in the thickness of the film. The ordered arrangement of the cavities has been formed by condensation of micrometric water droplets on the cooled evaporating surface of the forming films [9].

The obtained honey-like pattern has been reproduced by means of softlithography with polydimethylsiloxane and can be used in different kinds of applications [10].

We have found that copolymer **6** can give such kind of films with the same ordered pattern, even though the dimension of the holes is smaller and the distance among the holes is higher with respect to the films prepared only with polystyrene [4]. A typical picture of the morphology is reported in Fig. 4 where an optical micrograph of a film of **6**, obtained with the procedure reported in Ref. [4], is shown together with an AFM image of the same film.

A detailed study of the morphology of the film is under investigation and will be reported elsewhere. However preliminary data obtained by fluorescence microscopy indicates that the cavities as well as the surface of the film have a more intense emission with respect to the film obtained with PS homopolymer, indicating that the presence of EDOT oligo-

mers is homogeneously distributed. Moreover the edges of the holes on the film surface show an emission intensity which is higher with respect to the rest of the film indicating that a higher concentration of emitting species (EDOT oligomers) is present on the edge. These preliminary observation seems to be in agreement with the data already observed by other groups indicating that hydrophilic groups can be concentrated on the edge of the holes [11] or at the cavities surface [12].

4. Conclusions

We have presented a method to obtain copolymeric structures formed by a block of polystyrene, grown through ATRP, linked to a short sequence of styrene units substituted in para position by an EDOT unit. This copolymer can be used as an end capper for an EDOT polymerization. The structural and spectroscopical characterization performed have shown that segments of EDOTs with different lengths have grown starting from the EDOT units previously attached to styrene. This polymeric structure has been found to form, after evaporation of the solution in presence of moist air, thin films exhibiting ordered cavities on the surface. The presence of EDOT oligomers, linked to PS, was detected on both the surfaces of the film and in the cavities by investigation with fluorescence microscopy even though a higher intensity in the emission has been found from the edge of the cavities, in agreement with other observations on different systems.

Acknowledgments

This work was partially supported by Cariplo-PROTEO project; U.G. and A.B. thank Synergy RBNE03S7XZ project.

References

- [1] Hayakawa T, Horiuchi S. *Angew Chem Int Ed* 2003;42(20):2285–9.
- [2] Cui L, Han Y. *Langmuir* 2005;21(24):11085–91.
- [3] Fichet G, Corcoran N, Ho PKH, Arias AC, MacKenzie JD, Huck WTS, et al. *Adv Mater* 2004;16(21):1908–12.
- [4] Bolognesi A, Mercogliano C, Yunus S, Civardi M, Comoretto D, Turturro A. *Langmuir* 2005;21(8):3480–5.
- [5] Matyjaszewski K. *Chem Eur J* 1999;5(11):3095–102.
- [6] Tsolakis PK, Kallitsis JK, Godt A. *Macromolecules* 2002;35(15):5758–62.
- [7] Schmitt C, Nothofer HG, Falcou A, Scherf U. *Macromol Rapid Commun* 2001;22(8):624–8.

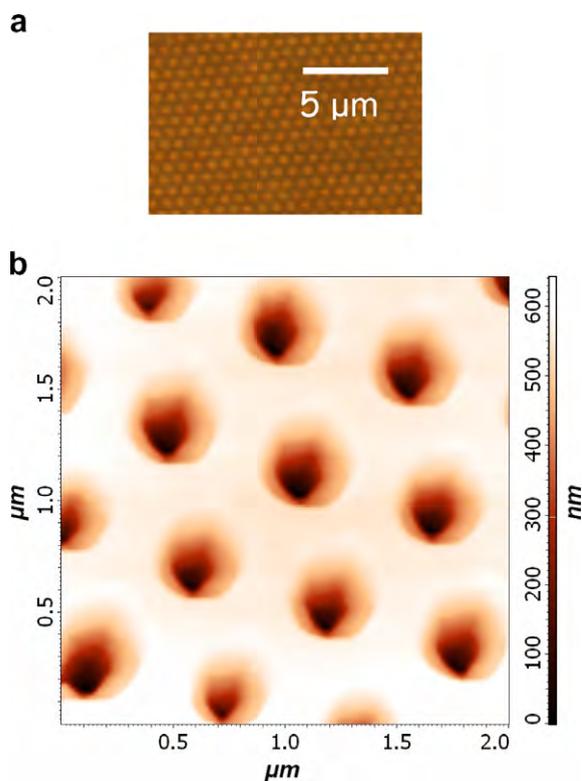


Fig. 4. (a) Optical microscopy picture of copolymer **6** film. (b) Height image of the thin film of copolymer **6**, AFM tapping mode. The AFM tip is unable to enter the holes on the surface so that the colour scale on the right gives an indication of the hole depth that can be detected by the tip.

- [8] Turbiez M, Frère P, Roncalli J. *J Org Chem* 2003;68(13):5357–60.
- [9] Bunz UHF. *Adv Mater* 2006;18(8):973–89.
- [10] Bolognesi A, Botta C, Yunus S. *Thin Solid Films* 2005;492(1–2):307–12.
- [11] Yunus S, Delcorte A, Poleunis C, Bertrand P, Bolognesi A, Botta C. *Adv Funct Mater* 2007;17(7):1079–84.
- [12] Böker A, Lin Y, Chiaperini K, Horowitz R, Thompson M, Carreon V, et al. *Nat Mater* 2004;3(5):302–6.