Influence of the Coil Block on the Properties of Rod−Coil Diblock Copolymers with Oligofluorene as the Rigid Segment

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ABSTRACT: Rod−coil diblock copolymers of 2-hydroxyethyl methacrylate (HEMA) with well-defined oligofluorene initiator were synthesized using the atom transfer radical polymerization (ATRP) technique. The resulting copolymers were characterized using spectroscopic (^{1}H NMR, GPC), optical (UV, photoluminesence), and thermal (DSC) techniques. The incorporation of the initiator into the polymeric chain was confirmed by spectroscopic methods, while strong evidence for microphase separation was obtained both from DSC and AFM. A detailed AFM study of the surface morphology in thin films was performed using rod−coil diblock copolymers having different flexible blocks, namely HEMA and polystyrene. Common solvents for both rod and coil blocks were used as a function of the solutions concentration of the diblock copolymers. By increasing the concentration of a selective solvent, formation of either islands, a stringlike morphology, and honeycomblike structures was observed. The optical properties of the HEMA copolymers from THF solution show no change in the emission spectra as we move from solution to the solid state. However, when ethanol was used as a solvent, a red shift of 10 nm was observed going from solution to the solid state, which is a strong indication for phase separation and organization of the diblock copolymers in alcoholic solutions. Annealing of the copolymers at 160 °C for 30 min resulted in green light emission due to the appearance of a new band at 535 nm in the case of OFPHM 6.0, while when polystyrene was used as coil block in OFPS copolymer pure blue light is emitted even after this treatment.

Introduction

From the materials scientist's point of view, rod−coil block copolymers with luminescent rod blocks are of special interest since it has been shown that the solid-state luminescence behavior of the conjugated rods can be fine-tuned.[1−9] Phase separation can occur in such systems because the rod and coil blocks are incompatible, having stiffness asymmetry which results in an increase in the Flory−Huggins χ parameter in comparison with coil−coil type diblock molecules. Phase-separated block copolymers can be further modulated with the use of different flexible block which differ on their hydrophobicity or hydrophilicity, their glass transition temperature, and their molecular weight. All these factors are expected to affect the final copolymer properties as well as their ability to self-organize in hierarchical structures.[10] A critical issue for these copolymers is the understanding of how their surface morphology influences their optoelectronic properties,[11] since spherical or cylindrical objects which are favorable for light-emitting applications and bicontinuous phases which are desirable in photovoltaic applications can be obtained from phase-separated organic semiconducting materials.

Unique morphologies have been observed, with a proper combination of the conjugated rod segments (poly(thiophenes),[6] poly(fluorenes),[7] and poly(phenylenes)[8] with hydrophilic and hydrophobic coil parts. Such morphologies include honeycomb structures,[2] mushroom-shaped nanostructures,[1] and nanowire structures.[9] Instead of using a conjugated polydispersed polymer block as the rod part in rod−coil block copolymers, it is preferable to use a monodispersed conjugated oligomer unit in which the conjugation length is well-defined and is effectively purified and characterized in respect to their spectral characteristics.[12] The resulting diblock copolymer would then combine the advantages of the oligomer approach in molecular electronics[13] such as solubility and well-defined conjugation length with those of polymers like easy processing, mechanical integrity, and absence of crystallization on devices. In addition, it would be very interesting to investigate how the use of oligomeric units instead of conjugated polymers influences the quantum efficiency in optoelectronic devices such as light-emitting diodes and photovoltaic applications.

Oligo- and polyfluorene as well as their derivatives are excellent candidates for optoelectronic applications because they exhibit high thermal and chemical stability and high fluorescence quantum yields in the solid state, emit blue light in both solution and solid state,[14−17] and in some cases show substantial charge carrier mobility.[18] The application of these materials is hindered by their tendency to produce green light either during annealing or upon passage of current.[19] Several attempts have been made in order to minimize or eliminate this undesirable phenomenon, with the use of dendrimers,[20] bulky substituents,[21] copolymerization techniques,[7b,22] and the oligomer approach.[19a,23] In a more recent work,[24] it was shown that blends of polyfluorenes with some nonconjugated polymers such as polystyrene or poly(vinyldiphenylquinoline) minimize the tendency of the polyfluorenes to produce green light.

In this paper, we present the synthesis of diblock copolymers using a monodispersed oligofluorene initia-

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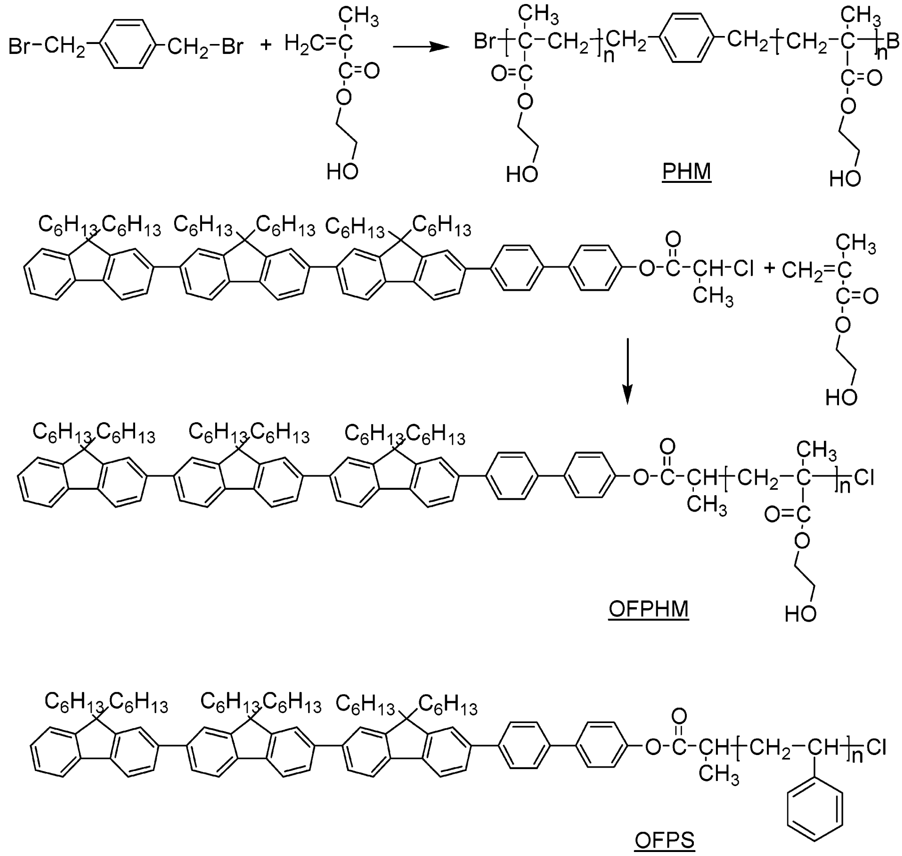
Scheme 1. Synthesis of HEMA Homopolymers (PHM) and Diblock Copolymers (OFPHM); Diblock Copolymer with Styrene as Monomer (OFPS) Is Also Presented



tor with HEMA via atom transfer radical polymerization (ATRP). The HEMA homopolymer is hydrophilic with a high degree of hydration but is not water-soluble. Therefore, a combination of hydrophobic conjugated oligofluorene segment coupled to the hydrophilic block of HEMA has attracted our interest because of the morphological behavior of the resulting copolymers in the solid state. A detailed morphological and optical characterization of the synthesized copolymers was performed, and the comparison to a diblock copolymer having the same rod part and hydrophobic polystyrene[5a] unit as the flexible block is also reported here.

Experimental Section

Materials. DMF was vacuum-distilled from finely powdered calcium hydride. HEMA was purified passing through a neutral silica column, eluted with 30/70 toluene/ethyl acetate, and distilled under reduced pressure. Copper(I) bromide (CuBr), 2,2′-bipyridine (bipy), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), methyl ethyl ketone (MEK), 2-propanol, and all the other reagents were used as received from Aldrich. All the polymerization reactions were run under an inert atmosphere (argon). The terfluorene macroinitiator was synthesized on the basis of a recently published procedure.[5a] Improvement of this procedure was achieved in the step of the synthesis of 2-bromo-9,9,9′,9′,9″,9″-hexahexyl-7,2′:7′,2″-terfluorene. The bromination reaction was carried out in chloroform for 2 h at 70 °C in the presence of ferric chloride and bromine, and the resulting precipitate was recrystallized from acetone instead of purification by column chromatography with 70% overall yield.

Measurements. The structures of the synthesized copolymers were clarified by high-resolution ^{1}H NMR spectroscopy with a Bruker Avance DPX 400 MHz spectrometer. Molecular weights (M_n and M_w) were determined by gel permeation chromatography (Ultrastyragel columns with 500 and 10^4 Å pore size; $CHCl_3$ (analytical grade) was filtered through a 0.2 μm Millipore filter; flow 1 mL min^{-1}; room temperature) using polystyrene standards for calibration. The samples were prepared as follows: Few grains of the copolymers dissolved first with a drop of dimethylformamide (DMF), and then chloroform solution was added. The UV spectra were recorded on a Hewlett-Packard 8452 A diode array UV−vis spectrophotometer. Fluorescence was measured on an SLM Aminco SPF-500 spectrofluorometer. Differential scanning calorimetry (DSC) thermograms were obtained using a TA Instrument DSC Q100 series. The heating rate was 10 °C min^{-1} for the first scan and 5 °C min^{-1} for the second scan, in a temperature region from −10 to 250 °C. Thin films of various concentrations (0.025, 0.125, 0.200, and 0.250 wt %) from alcoholic solutions of OFPHM 6.0 were prepared as follows: 1 mg of the OFPHM 6.0 was dissolved in 1 mL of EtOH 95% (0.125 wt %) and was filtered through a Millipore filter 0.25 μm. A drop of the filtered solution was deposited on a mica substrate and then spin-

Table 1. Reaction Conditions, Molecular Weight Characteristics, and Glass Transition Temperature of the Synthesized Homopolymers and Diblock Copolymers

polymer	monomer/ solvent (v/v)	M_n (GPC)	M_n (NMR)	PDI	T_g (°C)
PHM 7.6[a]	0.5	7 650		1.46	92.82
PHM 8.3[a]	0.5	8 300		1.45	92.60
PHM 26.8[b]	0.5	51 900		1.36	105.31
PHM 51.9[b]	0.5	84 200		1.85	108.96
OFPHM 6.0[a]	0.33	6 000	7 400	1.33	93.91
OFPHM 6.5[a]	0.33	6 500	7 500	1.35	94.88
OFPHM 17.6[a]	0.33	17 600	15 600	1.82	107.92
OFPHM 35.7[c]	2	35 700		1.63	
OFPHM 48.1[a]	2	48 100		1.63	110.23
OFPHM 67.5[b]	0.5	67 560		1.90	

[a] Reaction conditions: DMF, CuBr, bipy, 110 °C. [b] Reaction conditions: MEK/2-propanol (70/30 v/v), CuBr, bipy, 50 °C. [c] Reaction conditions: DMF, CuBr, bipy, 70 °C.

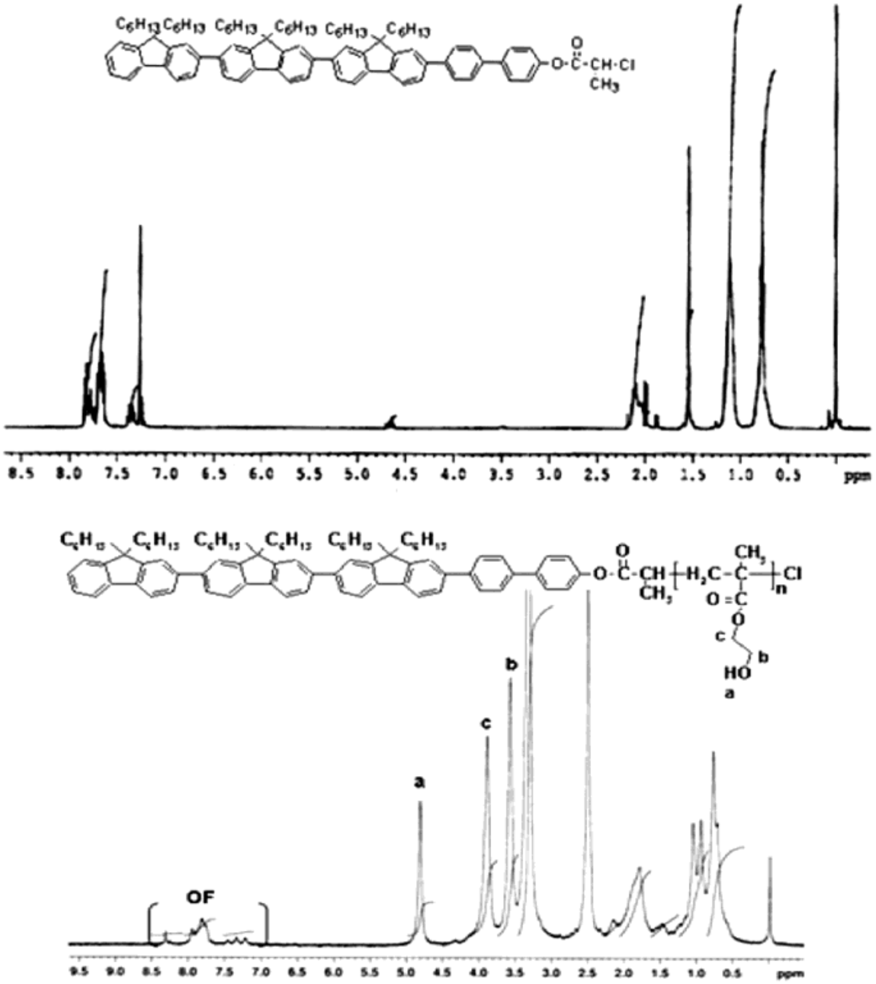


Figure 1. (a) ^{1}H NMR spectrum of the oligofluorene initiator in $CDCl_3$. (b) ^{1}H NMR spectrum of the diblock copolymer OFPHM 6.0 in d-DMSO.

coated. The mica surface is atomically flat, which precludes any influence of the substrate topography on the observed morphology. Imaging of the surface morphology of spin-coated samples was accomplished via AFM. A Topometrix Explorer SPM microscope (Theromicroscopes) equipped with a scanner of maximum ranges of 100 and 10 μm in *xy* and *z* directions, respectively, was used for the AFM measurements.

Synthesis of HEMA Homopolymers. A mixture of α,α-dibromo-*p*-xylene (0.1 mmol), CuBr (0.2 mmol), and bipy (0.4 mmol) was degassed and filled with argon. The solvent (1.5 mL) and the monomer (3 mL) were added with a syringe. The reaction mixture was heated (temperatures are specified in Table 1) for 18 h. The resulting brown solution turned green after exposured to air and addition of solvent (10−15 mL). Purification was achieved by passing the reaction solution through a silica column to remove the copper catalyst. Precipitation into ethyl acetate (20-fold excess by volume) removed traces of residual HEMA monomer and/or unreacted initiator, affording HEMA homopolymers as white powder.

Synthesis of HEMA Diblock Copolymers Using the Rigid Macroinitiator. A mixture of the oligofluorene initiator (0.1 mmol), CuBr (0.1 mmol), and bipy (0.2 mmol) or PMDETA (0.1 mmol) was degassed and filled with argon. The solvent and the monomer (quantities and temperatures are specified in Table 1) were added with a syringe. The reaction mixture was heated for 18 h. Purification was achieved by passing the reaction solution through a silica column to remove the copper catalyst. Precipitation into diethyl ether (20-fold excess by volume) removed traces of residual HEMA monomer and/or unreacted initiator, affording HEMA diblock copolymers as white powder.

Results and Discussion

The synthesis of oligofluorene-based diblock copolymers with HEMA as the flexible block was accomplished using atom transfer radical polymerization[25] of a properly modified oligofluorene initiator[5a] (Scheme 1). Different catalytic systems that are known to be effective for the ATRP of HEMA monomer, yielding polydispersities ranging from 1.09 to 1.8, were tested.[26] To effectively study different phase phenomena in block copolymers, low polydispersity is a prerequisite. In rod−coil block copolymers low polydispersities are also needed in order to study possible supramolecular assembly. The best results reported in the literature[26] with low polydispersities were obtained with CuBr/bipy as the catalytic system with mixed solvent systems such as methyl ethyl ketone (MEK):1-propanol (70:30 v/v) and methanol:H_2O (1:1 v/v) in low temperatures (20 and 50 °C). The results reported in Table 1 show that in our case the best catalytic system was proven to be that of CuBr/bipy with DMF as solvent in high temperatures (110 °C). For the homopolymerization of HEMA in DMF the results that reported in the literature show that polydispersities around 1.8 were obtained, indicating a rather poor living character of the system. Comparison of the literature results with the ones reported in Table 1 shows that the polydispersities in DMF at 110 °C for HEMA homopolymers were found to be around 1.46, which means that this system gives a better control of the polymerization in our case.

The incorporation of the initiator into the polymeric chain and the initiation efficiency were confirmed by ^{1}H NMR spectroscopy and size exclusion chromatography. In Figure 1, the ^{1}H NMR spectra of the initiator and the copolymer OFPHM 6.0 are presented. Most of the characteristic signals of the rigid block (Figure 1a) that are signals in the aromatic region of $\delta = 7.57-7.78$ ppm are clearly visible in the spectrum of the copolymer (Figure 1b). It is also evident that the signal at $\delta = 4.6$ ppm, which is assigned to the terminal protons next to the halogen atoms of the initiator, has totally disappeared after the polymerization. Size exclusion chromatography was used to confirm that no trace of the initiator is apparent in the copolymers and also to examine the effectiveness of the synthetic process in obtaining diblock copolymers with narrow polydispersities. Molecular weights were obtained using calibration based on polystyrene standards. Additional molecular weight determination was performed for the low molecular weight copolymers by ^{1}H NMR based on the signals of the different protons of the initiator and the PHM. More specifically, in the case of OFPHM 6.0, 6.5, and 17.6 the calculations were based on the comparison of the signal at 7.85 ppm due to the aromatic protons of the initiator with the signal at 3.88 ppm of the methylene protons in the β-position to the hydroxyl group of the polyHEMA block in the copolymer. The calculated values presented in Table 1 show that these results are in excellent agreement with the results obtained by SEC.

The thermal behavior of the synthesized initiator and copolymers has been studied by differential scanning calorimetry (DSC, Table 1). In Figure 2a, the oligofluorene initiator displays endotherms at 110 and 154.7 °C during the first heating scan possibly due to its liquid-crystalline behavior, while only a glass transition temperature (T_g) at 55.29 °C is obtained during the second heating scan. In Figure 2b, the DSC thermograms of the HEMA homopolymers and diblock copolymers are also depicted, indicating that both the T_g's of HEMA homopolymers as well as diblock copolymers are ranging between 92.6 °C for low molecular weights and 108.9 °C for the high molecular weights. Furthermore, the endotherms at 110 and 154.7 °C which correspond to oligofluorene initiator do not appear on the DSC thermograms for the diblock copolymers. As a result, we can conclude that the diblock copolymers are amorphous, a property that is desirable in cases where these materials will be used in the preparation of electronic devices in order to prevent crystallization in these devices. Phase separation of the diblock copolymers is evident from the DSC measurements. It found that the T_g of HEMA remains unchanged, supporting the existence of a pure HEMA phase, even though the T_g of the oligofluorene initiator which was incorporated in the copolymers as shown from the spectroscopic techniques was not observed even after annealing at 230 °C for 30 min.

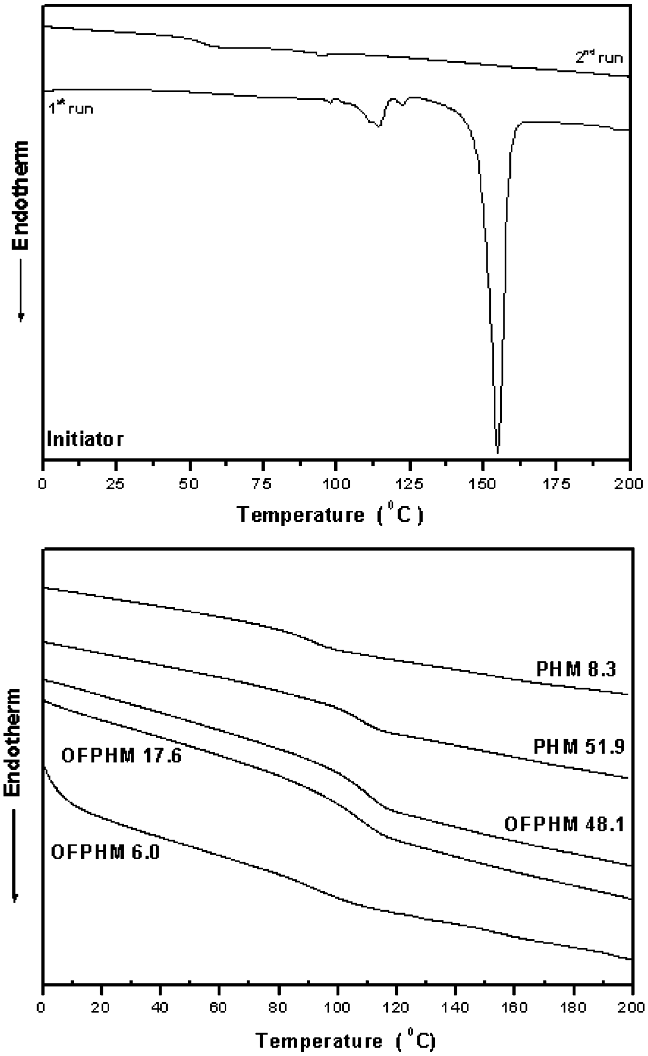


Figure 2. (a) DSC thermogram of the first and second heating scans for the oligofluorene initiator. (b) DSC thermograms of the second heating runs for the HEMA homopolymers and diblock copolymers, respectively.

An extensive study of the influence of the chemical structure of the coil segments is important for the understanding of the supramolecular organization in diblock copolymers containing oligofluorenes conjugated segments because of their tendency to form aggregates. Investigation of the self-assemble was achieved with the use of the AFM technique. OFPHM 6.0 was selected from the series of HEMA diblock copolymers with the various molecular weights for the study of the surface morphology because it contains 17.5% of the rod fraction in the polymer backbone and also has the lowest polydispersity (1.33). A selective solvent for the coil block was initially used. The structures formed from the above alcohol solutions in various concentrations are shown in the 5 × 5 μm images of Figures 3 and 4. In Figure 3a, a series of islands formed using solutions with the lowest concentration (0.025 wt %) are presented. These islands are distributed in all over the substrate and appear to align with each other. The average height of these islands is 9.62 nm whereas their width is 62.5 nm. At a higher concentration (0.125 wt %), the diblock copolymer forms a stringlike morphology as shown in Figure 3b. These string textures are 9.62 nm in height similar to those of islands and 125 nm in width. Interestingly, islands are continuing to appear into the strings which confirm the hypothesis that they tend to align with each other in some hierarchical way. Further increase in concentration at 0.200 wt % leads to a honeycomb-like texture as shown in Figure 3c. The characteristic dimensions of these honeycomb structures are 10 nm in height and 187 nm in width. In addition, the formation of islands is no longer observed for this concentration, which leads to a more homogeneous

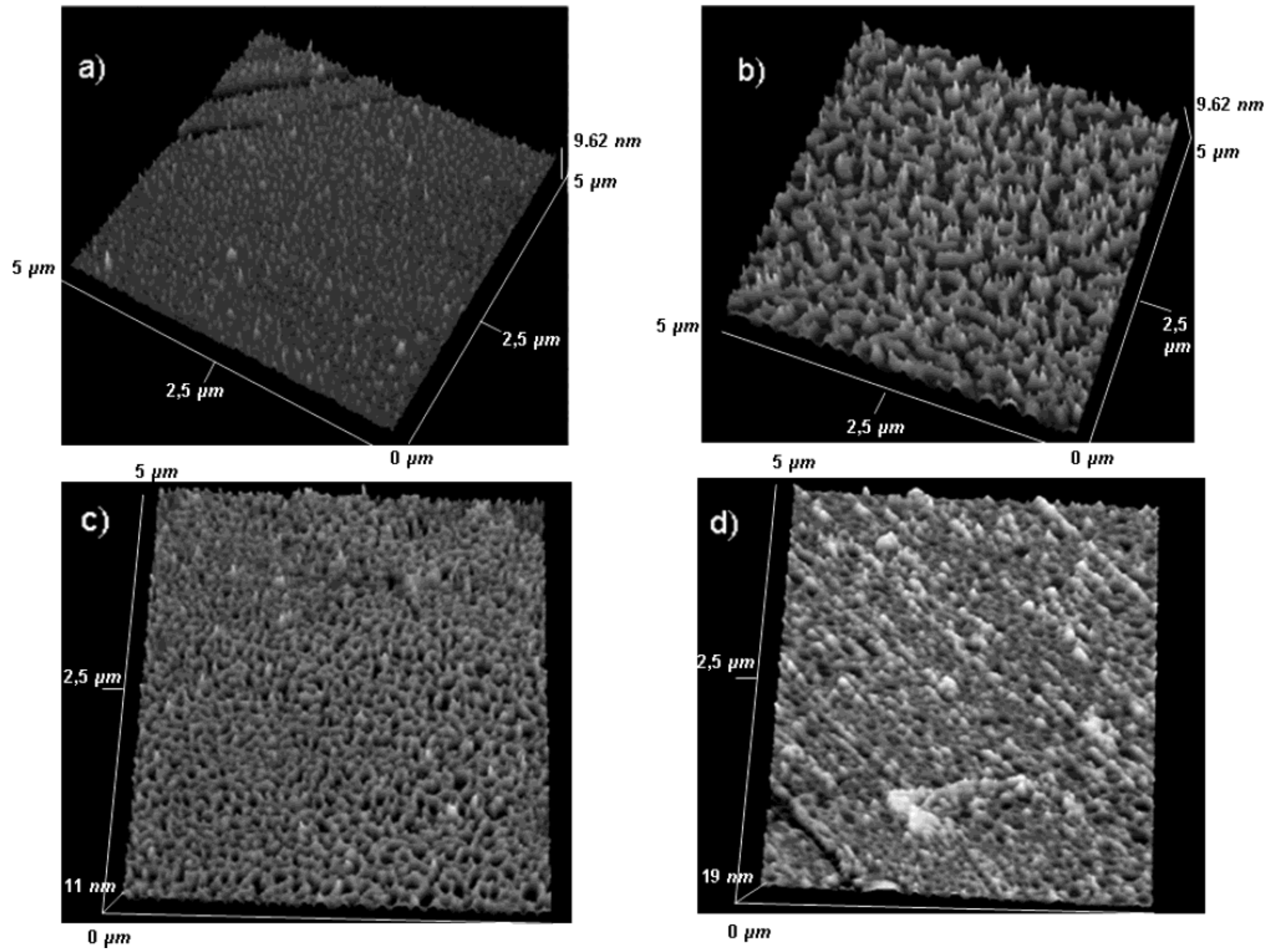


Figure 3. Three-dimensional rendering of (a) the island morphology from a solution of 0.025 wt %, (b) the stringlike morphology from a solution of 0.125 wt %, (c) the honeycomb morphology from a solution of 0.2 wt %, and (d) the honeycomb morphology from a solution of 0.25 wt %, observed by AFM (5 × 5 μm images) when OFPHM 6.0 was deposited on mica substrates.

structure. Finally, at concentration 0.250 wt % the honeycomb structure continues to be present as shown in Figure 3d. The width in this case is higher compared to the width of the sample from solution with concentration 0.200 wt %. The overall change in morphology is summarized in Figure 4 using a two-dimensional representation. These rod–coil diblock molecules form finite aggregates on the order of a few nanometers as revealed by atomic force microscopy, similar to the ones reported by Stupp.[1e]

By changing the solvent selectivity and using a common for both blocks solvent (THF) as in Figure 5a, the supramolecular organization still exists, but the structure is less perfect and with larger dimensions. To examine the influence of the coil block structure on the organization ability of these types of materials, diblock copolymers having polystyrene blocks as the coil part were also examined using AFM. Toluene was used as solvent this time, a common solvent for both blocks. The observed surface patterns at concentration 0.060 wt % are presented in Figure 5b,c. In this case, honeycomb-like structures were also obtained, showing that the change of the coil block structure does not disturb the ability to self-organize but only affects the size of the structure formed. The characteristic dimensions are 23 nm in height and 257 nm in width for the OFPS copolymer in this case. On the basis of the above results, we can say that when a selective solvent for the coil blocks is used, the tendency of the block copolymer to self-assemble is enhanced due to the phase separation and the aggregation of the rigid segments. The observed here surface patterns can be considered as hierarchical structures resulting from the stacking of ribbonlike nanostructures formed from the two phase-separated blocks.

Finally, the optical properties of the oligofluorene initiator and its HEMA diblock copolymers were investigated with absorption and emission spectroscopy both in solution and in solid state. In Figure 6, the absorption spectra of the initiator and the diblock copolymers in solid state from THF solutions are compared. The absorption intensities of these copolymers at 295 and 360 nm in solid state are attributed to the HEMA and oligofluorene block, respectively. The oligofluorene absorption peak is decreases as the molecular weight increases due to the fact that the percentage of the oligofluorene part in the polymeric chain decreases as well. However, the transition from solution to the solid state in THF did not affect the emission properties of the OFPHM 6.0 as shown in Figures 7 and 8. The fact that the emission spectra of the initiator and OFPHM 6.0 are almost the same in THF, which is a good solvent for both blocks, shows that the flexible chain does not affect the luminescent properties of the chromophore. Similar cases in which the emission spectra of polyfluorene derivates in solution and in the solid state are quite similar have been recently reported.[5a,27]

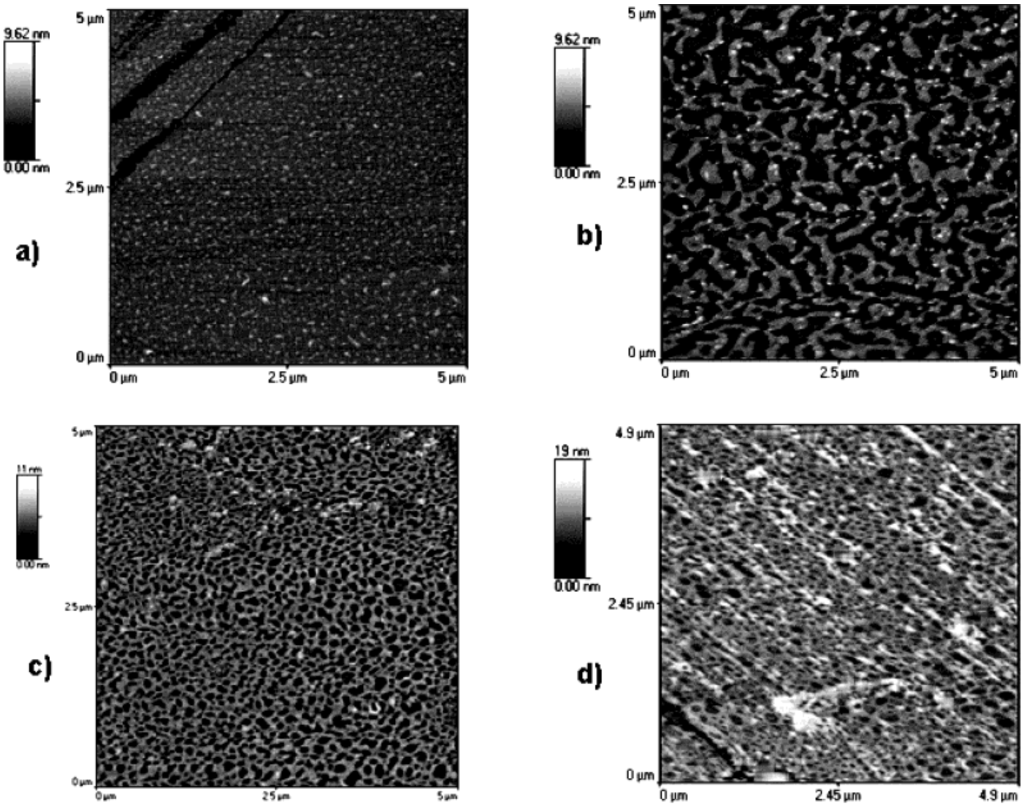


Figure 4. AFM micrographs of surface patterns formed by the OFPHM 6.0 on mica substrates as a function of solution concentration: (a) 0.025, (b) 0.125, (c) 0.2, and (d) 0.25 wt % Each image is a 5 × 5 μm tapping-mode AFM scan.

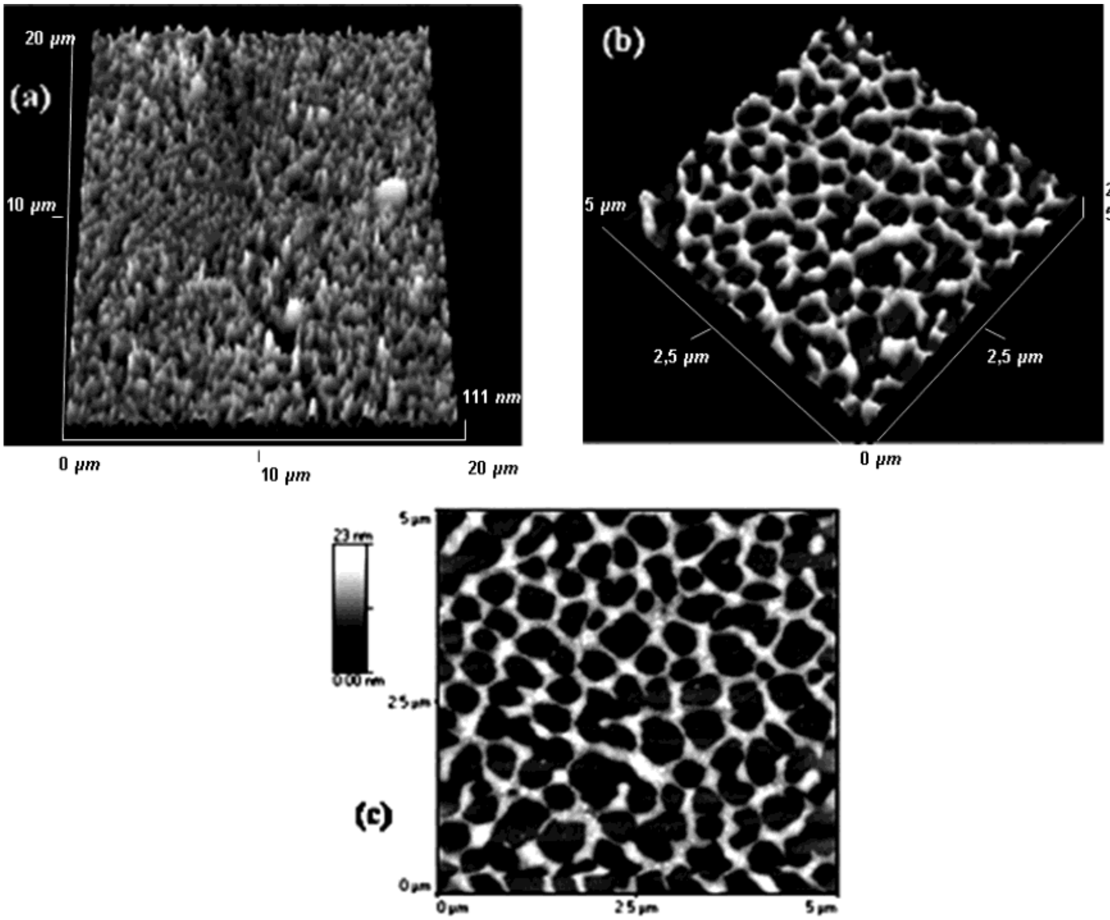


Figure 5. AFM micrographs of (a) OFPHM 6.0 in THF solution at 0.125 wt % (three-dimensional 20 × 20 μm tapping-mode AFM scan), (b) OFPS in toluene solution at 0.060 wt % (three-dimensional 5 × 5 μm tapping-mode AFM scan), and (c) OFPS in toluene solution at 0.060 wt % (surface pattern 5 × 5 μm tapping-mode AFM scan) on mica substrates.

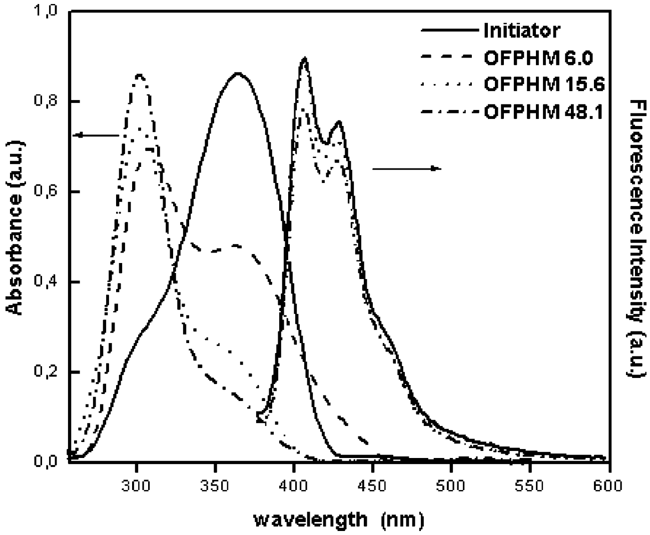


Figure 6. UV−vis absorption and photoluminescence spectra of the oligofluorene initiator and the diblock copolymers OFPHM 6.0−15.6−48.1 as thin films cast from THF. Excitation wavelength was 360 nm.

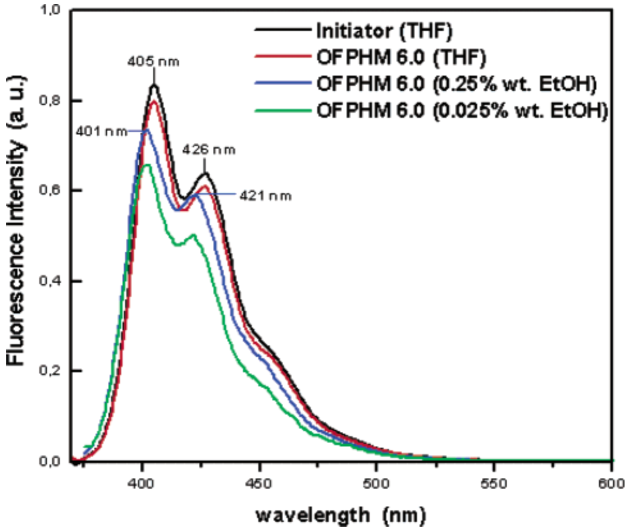


Figure 7. Photoluminescence spectra of the oligofluorene initiator and OFPHM 6.0 in THF solution and OFPHM 6.0 as a function of concentration in EtOH 95% solution.

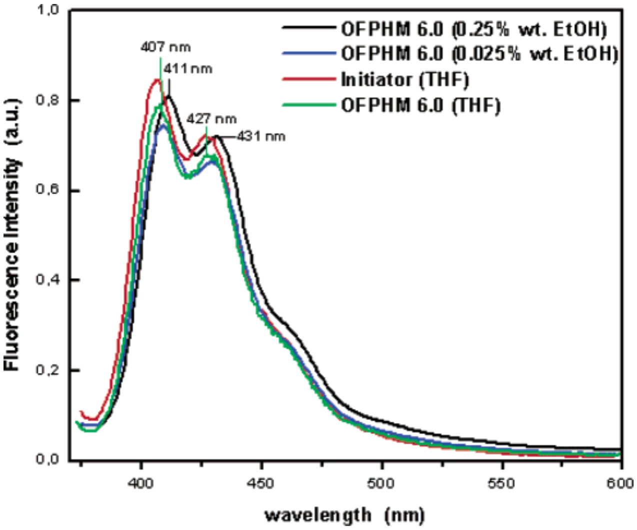


Figure 8. Photoluminescence spectra of the oligofluorene initiator and OFPHM 6.0 in solid state from THF and OFPHM 6.0 as a function of concentration in solid state from EtOH 95%.

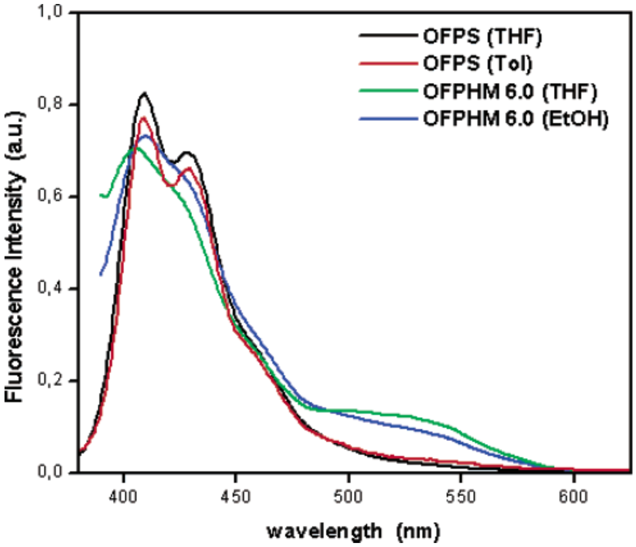


Figure 9. Photoluminescence spectra of the OFPS and OFPHM 6.0 in solid state from different solvents after annealing in air at 160 °C for 30 min.

The emission spectra of the OFPHM 6.0 in solution and in solid state in conditions similar to those reported for the AFM measurements are presented in Figures 7 and 8. In addition, when EtOH 95% was used as solvent instead of THF, the emission properties changed as we moved from solution to the solid state. Figure 7 show that there is a red shift of 5 nm in the emission bands of the OFPHM 6.0 in solution when THF is used instead of EtOH 95%. No significant changes in the solid state were found when THF was used as solvent as seen in Figure 8. However, when EtOH 95% was used, a red shift by 10 nm was observed going from solution to the solid state as shown in Figures 7 and 8. Comparing the thin films deposited from THF and EtOH, almost the same spectra for both THF and the diluted EtOH solution (0.025%) were obtained. When higher concentration was used in EtOH (0.25%), the formed film shows evidence of aggregation as supported by the red shift of the spectra (Figure 8). In the case when the good solvent for the flexible block (EtOH 95%) is used, it is observed that the coil chain affects the luminescent properties of the chromophore unit. The intermolecular packing of the oligofluorene block is allowed in this case into well-organized aggregates. These results are in agreement with the AFM measurements reported earlier in this paper.

Support for the fact that some of the studied here block copolymers are capable of producing pure blue light after thermal treatment comes from studies where we investigated their thermal resistance toward aggregate formation in the solid state. The results of the annealing of the above copolymers in air for 30 min at 160 °C (a temperature much higher than the T_g's of both HEMA and styrene) are depicted in Figure 9. It is evident that the OFPHM 6.0 copolymer casted as thin film in both solvents (THF, EtOH 95%) exhibits the appearance of a low-intensity broad band in the emission spectrum at 535 nm which is attributed to the formation of aggregates. However, this emission band was not observed in the case of the OFPS copolymer. In both cases the used oligofluorene block was synthesized using the same chemistry and purification processes so as any observed difference on their optical behavior can safely be attributed to the presence of the flexible blocks and consequently to their influence on the organization of the copolymers[4,28] and not to any other chemical changes as the formation of keto defects, which also explain the creation of the band at 535 nm in polyfluorenes as was reported in other cases.[7a,12b] The only difference in our case is that we did not use polyfluorenes as the rigid segment but well-defined, purified, and spectroscopic characterized oligofluorene blocks. All the above discussion shows that the OFPS block copolymers are ideal candidates for the application in organic light-emitting diodes as blue emitters. The only concern about the use of these materials is the fact that the flexible block may hinder charge transport and thus prevent the observation of electroluminescence. However, recent work[24] has conclusively shown that good blue LEDs can be made from polyfluorene/polystyrene blends. Therefore, the selection of the proper flexible block is essential for the stabilization of the emission spectra of oligofluorene copolymers, as was clearly demonstrated in this work.

Conclusions

Rod−coil diblock copolymers of 2-hydroxyethyl methacrylate (HEMA) with monodispersed oligofluorene initiator were synthesized using an ATRP technique. The best catalytic system was proven to be CuBr/bipy with DMF as solvent at 110 °C. The incorporation of the initiator in the polymer backbone was confirmed using the ^{1}H NMR and size exclusion chromatography. The T_g of HEMA was found in the diblock copolymers whereas no T_g of the initiator was appeared even after annealing of the copolymers. Major differences in the morphologies of the OFPHM 6.0 were obtained as a function of change in concentration in alcoholic solutions. At low concentrations (0.025 wt %), the nanostructures form islands. As concentration increases (0.125 wt %), a stringlike morphology is observed, and finally at higher concentrations (0.200 wt %) the copolymer exhibits a honeycomb morphology. Furthermore, the emission properties of the copolymers in THF did not change passing from solution to the solid state. In contrast, when EtOH 95% was used as solvent, the transition from solution to the solid state altered the emission properties of OFPHM 6.0. Finally, the proper selection of the coil block resulted in pure blue light emission even after the application of extensive thermal treatment.

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