

Thermally Stable Blue Emitting Terfluorene Block Copolymers

Christos L. Chochos,^{†,‡} Joannis K. Kallitsis,^{†,‡} Panagiotis E. Keivanidis,[§]
Stanislav Balushev,[§] and Vasilis G. Gregoriou^{*,†}

Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High-Temperature Processes (FORTH-ICEHT), P.O. Box 1414, Patras 26500, Greece, Department of Chemistry, University of Patras, Patras 26500 Greece, and Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

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Spectroscopic and morphological studies on a series of rod–coil block copolymers containing terfluorene segments as the rigid blocks and polystyrene as the flexible parts demonstrate an increase in the photoluminescence intensity and the exciton lifetime as well as formation of isolated spheres as thin films upon thermal annealing in air (200 °C for 30 min). Moreover, no appearance of the low energy emission band centered at 520 nm was found after the same thermal treatment which permits these copolymers to emit pure blue light.

1. Introduction

Polyfluorenes (PFs)^{1–3} have emerged as an attractive class of electroluminescent conjugated polymers for use in blue light emitting diodes (LEDs), exhibiting high photoluminescence quantum yields in the solid state. However, the major disadvantage of PF-based LEDs is their poor spectral stability under normal operation with the appearance of a low-energy emission band occurring at 520–530 nm.⁴ Several attempts have been made to stabilize the blue color emission using either dendrimers,⁵ bulky substituents⁶ in the 9-position of the fluorene moiety, copolymerization techniques,^{7,8} purification of the fluorene monomers before polymerization,⁹ or blends of polyfluorenes with some nonconjugated polymers such as polystyrene or poly(vinyl diphenylquinoline),¹⁰ but the green electroluminescence band was not eliminated.

So far, different models have been proposed to explain the origin of the green emission band centered at 520–530 nm; however, none has yet conclusively resolved the exact nature of the emission. Some research groups suggest that the low-energy emission band is attributed to the formation of aggregates and/or intermolecular excimers.^{1,7,11,12} In addition, the emission from isolated fluorenone defects on polyfluorene chain, rather than intermolecular aggregates or excimers, was proposed as a possible mechanism for the appearance of the green emission band.^{3,13–16} These fluorenone defects could be formed either during polymerization or later by thermal or photooxidation of polyfluorene films at the monosubstituted C9 sites of the fluorene unit.^{9,15,17} Within this context, theoretical calculations have concluded that the low-energy green emission band is a consequence of exciton trapping¹⁸ on fluorenone sites that is followed by a charge-transfer π – π^* radiative transition¹⁹ to the ground state. Recently, the charge-transfer nature of this emission was experimentally confirmed as it was found to

exhibit solvatochromic effects.²⁰ Moreover, thermally induced cross-linking reaction steps have also been identified as the origin for the low energy emission band.²¹

However, a new hypothesis was made, claiming that fluorenone alone is a necessary but not sufficient condition for the appearance of this undesirable low energy emission band.^{22,23} It was shown that interchain/intersegment interactions are required for the appearance of the green emission band in the photoluminescence spectra of polyfluorenes and the argument made was that the low energy band at 520–530 nm is attributable to emission from fluorenone-based excimers rather than from localized fluorenone n – π^* transitions.

Since high chemical purity and structural uniformity are considered critical factors for PLED performance, monodispersed conjugated oligomers are used instead of conjugated polymers. Therefore, the use of rod–coil block copolymers with a monodispersed conjugated oligomeric unit as the rigid segment and some nonconjugated molecule as the flexible block is one approach for the incorporation of well-defined oligomeric segments into polymer backbone. Moreover, the resulting block copolymers should combine the advantages of the oligomer approach in molecular electronics such as solubility and well-defined conjugation length with those of polymers such as easy processing, mechanical integrity and absence of crystallization in devices.²⁴ Even though there are many reports depicted in the literature^{25–31} involving rod–coil block copolymers incorporating polyfluorenes as the rigid block, only a few studies^{11,32} featuring monodispersed oligofluorenes as the rod part have been presented.

Therefore, in this work, we present the influence of the thermal treatment on the optical properties and the surface morphology in a series of block copolymers consisting of terfluorene segments and polystyrene flexible parts as thin films and we propose the block copolymer approach as an alternative solution for the elimination of the undesirable green emission band centered at 520–530 nm in polyfluorenes. Rod–coil diblock copolymers having a well-defined terfluorene unit as the rigid segment and polystyrene as the flexible part TFPS(I) and -(II) show an increase of the photoluminescence intensity

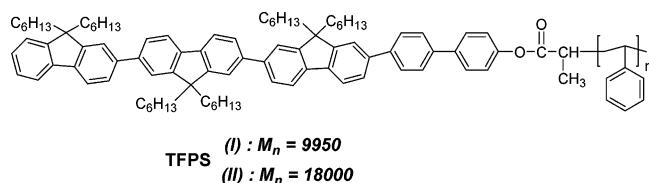
* Corresponding author. Telephone: (+30)2610-965205. Fax: (+30)2610-965223. E-mail: gregoriou@iceht.forth.gr.

[†] Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High-Temperature Processes (FORTH-ICEHT).

[‡] Department of Chemistry, University of Patras.

[§] Max Planck Institute for Polymer Research.

SCHEME 1. Molecular Structure of the Diblock Copolymers TFPS(I) and -(II)



and the exciton lifetime without the concurrent appearance of the green emission band upon thermal annealing compared to polyfluorenes. Our group have recently demonstrated²³ the impact of the photooxidation treatment on the optical properties of the same block copolymers TFPS(I) and -(II). These materials continue to emit pure blue light even after the photooxidation treatment and formation of the fluorenone moiety without the appearance of the low energy emission band centered at 520–530 nm. Thus, these copolymers possess very promising optical properties for application in polymeric light-emitting diodes.

2. Experimental Section

Materials. The diblock copolymers TFPS(I) and -(II) (Scheme 1) were synthesized based on published procedure.³² The weight percentages of terfluorene segment in the TFPS(I) and TFPS(II) are 13.1 and 7.2, respectively.

Instrumentation. Gel permeation chromatography (GPC) measurements were carried out using a polymer lab chromatographer with two Ultra Styragel linear columns (10⁴, 500 Å), UV detector polystyrene standards and CHCl₃ as eluent, at 25 °C with a flow rate of 1 mL/min. Continuous wave photoluminescence (cw-PL) was measured on a Perkin-Elmer LS45 spectrofluorometer. FT-IR spectra were recorded with a Nicolet Magna 850 spectrometer equipped with an MCT/A detector. For the FT-IR and cw-PL measurements thin films from chloroform or toluene solutions of both 0.24 and 10 mg/mL were spin-coated at a rotational speed of 2000 rpm and rotation duration time of 60 s on barium fluoride (BaF₂) and quartz substrates, respectively. Thermal annealing was performed at 200 °C for 30 min in air for both the FT-IR and cw-PL measurements, respectively. For the time-resolved photoluminescence (TR-PL) experiments, excitation of the samples took place with a frequency-doubled mode-locked Ti:Saph laser, producing pulses of approximately 200 fs duration, operating at a repetition rate of 80 MHz. The collected PL signal was dispersed by a 0.25 m monochromator with a 50 lines/mm grating and detected with a Hamamatsu C4742 streak camera. During the measurement time the samples were kept under vacuum, in a continuous coldfinger liquid nitrogen cryostat. For room-temperature measurements the thin films were kept under a dynamic vacuum of 10⁻⁴ mbar. TR-PL studies were performed in pristine and annealed films of the materials. Thin films of the materials were prepared on cleaned quartz substrates via spin-coating at a rotational speed of 1200 rpm and rotation duration time of 60 s. The solution used for spin-coating process was of a concentration of 10 mg/mL prepared in degassed toluene. In the case of TFPS(I) films, annealing took place by the deposition of a pristine film in an oxygen containing oven at 170 °C for approximately 12 h. Subsequently, the film was rapidly exposed at room temperature. For TFPS(II), annealing of the films took place by positioning the prepared film on an electronically controlled one-stage Peltier element, in a chamber. The pristine films were heated for an hour at 105 °C either by letting the chamber opened and exposed to air or by keeping it sealed in a dynamic vacuum of 10⁻⁴ mbar. In the case of

TFPS(II), the sample annealed in a vacuum, the chamber was kept under high vacuum until the temperature had reached room temperature values. In such a way, we excluded the impact of oxygen due to thermally activated processes. Imaging of the surface morphology of spin-coated samples was accomplished via AFM. A Topometrix Explorer SPM microscope (thero-microscopes) equipped with a scanner of maximum ranges of 100 and 10 μm in xy and z directions, respectively, was used for the AFM measurements.

3. Results and Discussion

3.1. FT-IR Spectroscopic Characterization. The FT-IR spectra of the thermally treated diblock copolymers as thin films in the 1800–1700 cm⁻¹ region are presented in Figure 1. The thermal annealing of TFPS(I) and -(II) at 200 °C for 30 min in air reveals no generation of the 1726 cm⁻¹ band assigned to the carbonyl stretching mode of the fluorenone moiety.³³ Even though the appearance of the fluorenone unit after extensive thermal treatment in polyfluorenes is well documented,^{34,35} the terfluorene segment in our block copolymers do not exhibit the formation of the fluorenone moiety after thermal annealing at 200 °C for 30 min in air. This result is in agreement with the findings of the TR-PL which are presented next in the text.

3.2. Continuous Wave and Time-Resolved Photoluminescence Properties. To investigate the influence of the thermal treatment on the optical properties of the synthesized diblock copolymers, we studied their photoluminescence spectra as pristine films, casted from two different solvents (toluene and chloroform) and after thermal annealing. Not only did the cw-PL characteristics of TFPS(I) and -(II) remain unaltered upon thermal annealing at 200 °C for 30 min in air but also an increase in the emission intensity was observed (Figure 2a). Similar results on the emission spectra of TFPS(I) and -(II) before and after the application of the same thermal treatment were revealed when these materials casted from toluene solutions. For example, the emission spectra of TFPS(I) casted from toluene solution at concentration of 0.030wt % before and after thermal annealing at 200 °C for 30 min in air are presented in Figure 2b. An increase in the emission intensity of TFPS(I) was also observed (Figure 2b). In addition, no appearance of the low energy emission band at 520 nm was observed, with these materials continuing to emit pure blue light even after this extensive thermal treatment. However, when the type of the flexible block was changed to poly(2-hydroxyethyl methacrylate) instead of polystyrene, the emission properties of the same terfluorene segment changed after thermal annealing¹¹ (the appearance of the low energy emission band at 520 nm was detected). The used terfluorene segment was synthesized with the same chemistry and purification processes in both rod-coil block copolymers (polystyrene and poly(2-hydroxyethyl methacrylate)). Therefore, while the fluorenone moiety (one of the reasons for the appearance of the low-energy green emission band as was mentioned in the Introduction) is not generated upon annealing of the terfluorene segment (Figure 1 and the results obtained from the study of TR-PL technique), any observed difference on the optical properties of the copolymers can safely be attributed to the presence of the flexible parts. Thus, we attribute the fact that TFPS(I) and -(II) can effectively inhibit the appearance of the low energy green emission band to the presence of the polystyrene flexible block even at high temperatures in air.

With the aim of understanding the increase of the emission intensity of TFPS(I) and -(II) we proceeded to further studies with the use of TR-PL technique. Annealing of TFPS(II) was

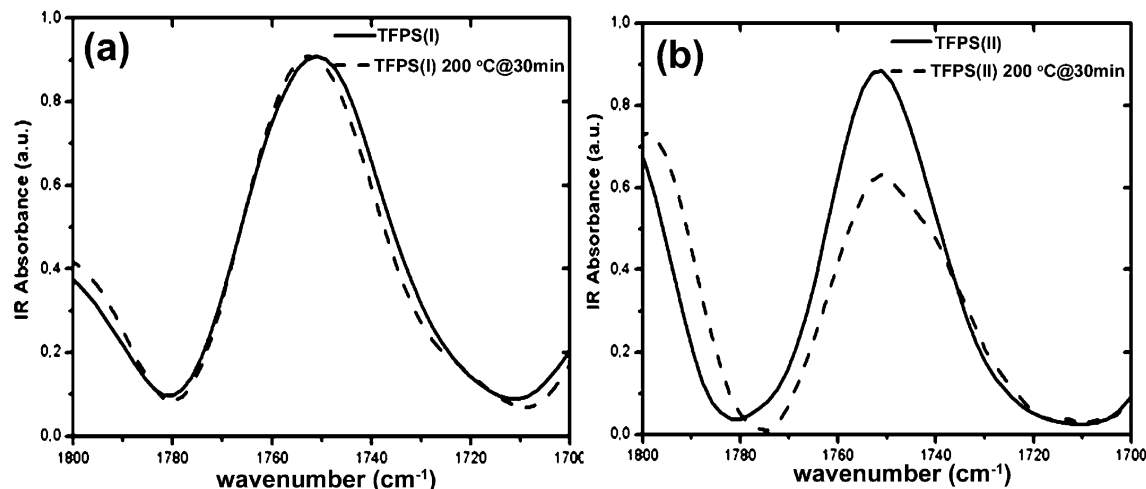


Figure 1. FT-IR spectra in the 1800–1700 cm^{-1} spectral region of (a) TFPS(I) and (b) TFPS(II) as pristine films and after thermal annealing (200 $^{\circ}\text{C}$ for 30 min) in air.

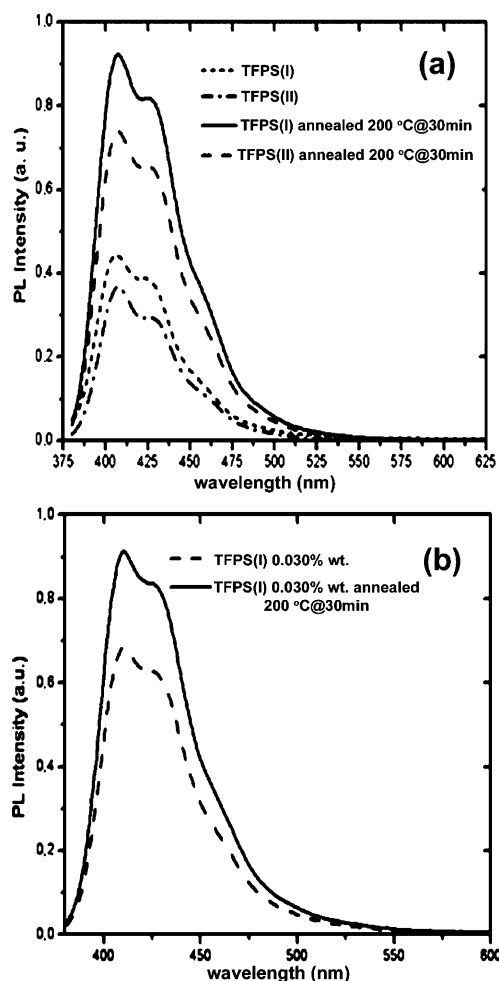


Figure 2. (a) Photoluminescence spectra in arbitrary units of TFPS(I) and -II) in the solid-state casted from chloroform solutions, before and after thermal annealing (200 $^{\circ}\text{C}$ for 30 min) in air. (b) Photoluminescence spectra in arbitrary units of TFPS(I) in the solid-state casted from toluene solution at concentration of 0.030 wt % before and after thermal annealing (200 $^{\circ}\text{C}$ for 30 min) in air. Excitation wavelength was 360 nm.

done at 105 $^{\circ}\text{C}$ (a temperature slightly above the glass transition temperature T_g of the copolymer) both in air and vacuum. In the case of TFPS(I), the annealing conditions were performed at 170 $^{\circ}\text{C}$ (a temperature much higher than the T_g of the

copolymer) in air. Figure 3a presents the time-resolved photoluminescence spectra for a pristine and an annealed film of TFPS(I) in air. The spectra correspond to a ~ 2 ns delay after excitation of the films. In both samples, a significant emission intensity is observed at 480 nm that is comparable to that of the singlet delayed emission intensity. Such emissive features have been attributed to the existence of interchain species in the films of PFs,¹⁶ that are apparently related to the solid-state morphology.

In agreement with the results of the cw-PL of Figure 2a, an increase in the lifetime of the blue emission intensity is clearly observed after the annealing process of the films. Figure 3b presents the PL decay curves of TFPS(I) both for pristine and annealed in air films. The PL transients monitor the 420–450 nm spectral region. No differences were observed in comparison to the corresponding transients of the 400–420 nm region. A very similar trend for increase in lifetime of the blue emission intensity, after annealing, was observed for the thin films of TFPS(II). As the inset of Figure 3b shows, annealing of a TFPS(II) film in a vacuum results in prolongation of the blue emission intensity.

One has to distinguish between the origins of the two potential defect sites in a polymeric film. Structural defects related to film morphology can be present that are different in nature than chemical defects (e.g., fluorenone). Since an indication for the existence of a structural defect spectral features exists both in a pristine and an annealed film of TFPS(I) (Figure 3a), the fact that an increase of the excited state lifetime is observed after annealing in air should reflect a reduction of structural defects upon annealing. This is due to an induced ordered morphology in the film after annealing that will subsequently reduce the number of structural defects, thus prolonging the lifetime of the excited state. Alternatively, in the presence of chemical defects onto the molecular backbone, an induced order would lead to a decrease of the excited-state lifetime due to an enhanced assistance of the photoexcitation migration toward the photoluminescence quenching centers. Therefore, as the chemical defects seem to remain unaltered for both the copolymers TFPS(I) and -II) after annealing, a result similar to the findings obtained from the FT-IR study (Figure 1), the concentration of structural defects in TFPS(I) and -II) has decreased.

3.3. Morphological Characterization. An extensive study of the surface morphology of the diblock copolymers consisting of terfluorene segments as the rod block and polystyrene as the

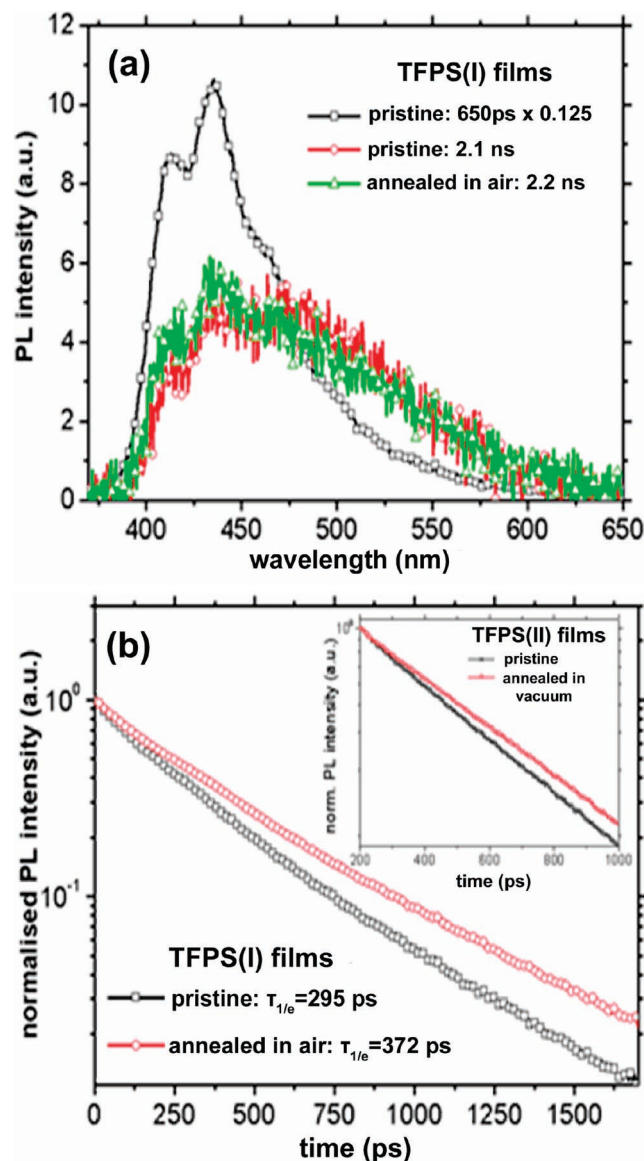


Figure 3. (a) Time-resolved photoluminescence spectra for a pristine and an annealed in air film of TFPS(I) casted from toluene solution. (b) Photoluminescence decay curves of the blue emission region of TFPS(I) before and after thermal annealing in air. In the inset, the photoluminescence decay curves of the blue emission of TFPS(II) as pristine and annealed in a vacuum are presented. For both TFPS(I) and TFPS(II) the PL transients, monitor the 420–450 nm spectral region. Excitation wavelength was 380 nm.

flexible part was performed using the AFM technique. Surface patterns of TFPS(I) and -(II) as thin deposits and after annealing are presented in Figures 4–6. In a previous work,¹¹ it was shown that TFPS(I) was able to self-assemble in honeycomblike structures at concentrations 0.060 wt % from toluene solutions. Therefore, it would be very interesting to examine the influence on the overall surface morphology of the rod–coil diblock copolymers containing terfluorene and polystyrene segments respectively, the change of the solution concentration, the selection of the solvent (toluene vs chloroform), the percentage of the rod block as well as the thermal treatment at 200 °C for 30 min in air. Finally, it is also very important to undertake a detailed study of the relationship between the luminescence properties and the thin film morphologies which could give useful information and establish a better correlation of the photophysical properties with the sample morphology of the studied diblock copolymers.

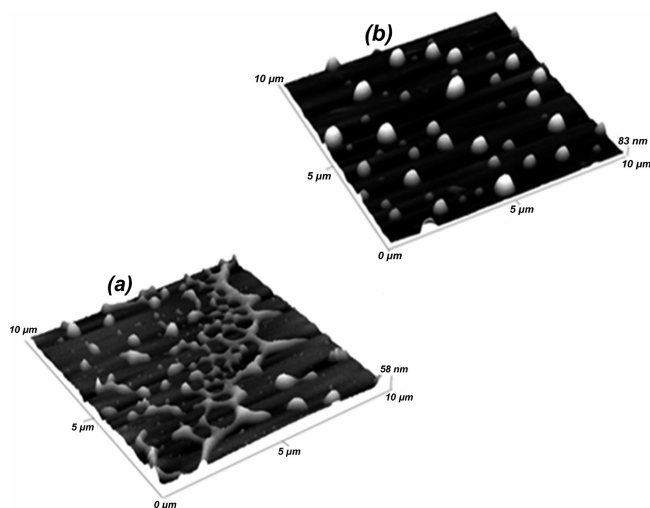


Figure 4. AFM micrographs of surface patterns formed by the TFPS(I) at 0.030 wt % (from toluene solution) on mica substrates (a) as pristine film (three-dimensional $10 \times 10 \mu\text{m}^2$ tapping-mode AFM scan) and (b) after thermal annealing at 200 °C for 30 min in air (three-dimensional $10 \times 10 \mu\text{m}^2$ tapping-mode AFM scan).

By changing the concentration of TFPS(I) to 0.030 wt % from toluene solution, large areas of irregular structures and spherical domains on the order of 600 nm are observed as shown in Figure 4a. From our previous work,¹¹ it is known that going to higher concentration (0.060 wt %), the observed honeycomblike structures result from the alignment of these spherical domains into organized structures. The surface morphology of Figure 4a can be described as the formation of aggregates in a micrometer scale ($10 \times 10 \mu\text{m}^2$ imaged area) which does not influence the color purity of TFPS(I) (no appearance of the low energy emission band as shown in Figure 2). This observation is in agreement with the result obtained from the TR-photoluminescence (Figure 3a) which showed an emission intensity at 480 nm assigned to interchain aggregates. Similar morphology has also been observed for a polyfluorene consisting of 75% dihexyl and 25% ditriphenylamine side chain groups.¹² After thermal annealing at 200 °C for 30 min in air only spherical domains on the order of 700 nm in width are observed based in Figure 4b. The results obtained here after thermal application are similar to the ones reported in previous works for a 50% polyfluorene(PFO): 50% polystyrene(PS) blend annealed at 100 °C (formation of perfectly spherical domains was also observed with diameters of 2–15 μm)¹⁰ and a triblock copolymer containing a polyfluorene segment as the rigid block and polythiophenes as the flexible parts.³⁶ For the case of TFPS(I), the change of the surface morphology after annealing seems to be responsible for the increase of the emission intensity of TFPS(I), as well as for the increase of the excited-state lifetime based from the results of Figure 3b which were proposed to be a reduction of the concentration of the structural defects after thermal treatment.

The selection of solvent seems to differentiate the morphology of the TFPS(I) copolymer in the solid state. The surface morphology of TFPS(I) at concentration 0.030 wt % from chloroform solution exhibits finer phase separation (Figure 5a) in contrast to toluene (Figure 5b). Formation of nanometer features were created for TFPS(I) in the case of chloroform in contrast to the appearance of the irregular structures and spherical domains when toluene was used as solvent. A possible explanation for the observation of the different morphologies of TFPS(I) is the dissimilar volatility of the two solvents. However, after the application of thermal annealing at 200 °C

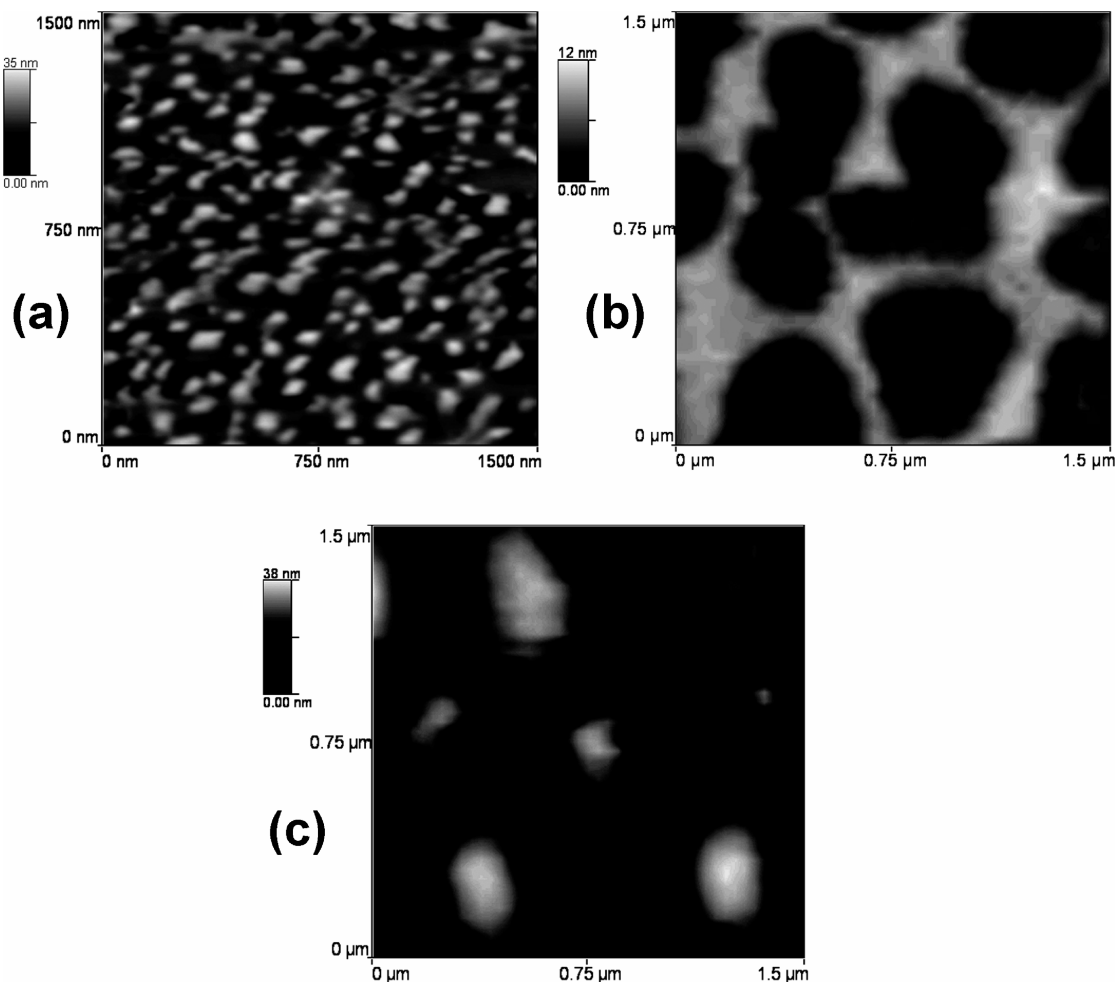


Figure 5. AFM tapping-mode micrographs of surface patterns formed by the TFPS(I) at 0.030 wt % (a) from chloroform solution, (b) from toluene solution, and (c) after thermal annealing at 200 °C for 30 min in air from chloroform solution.

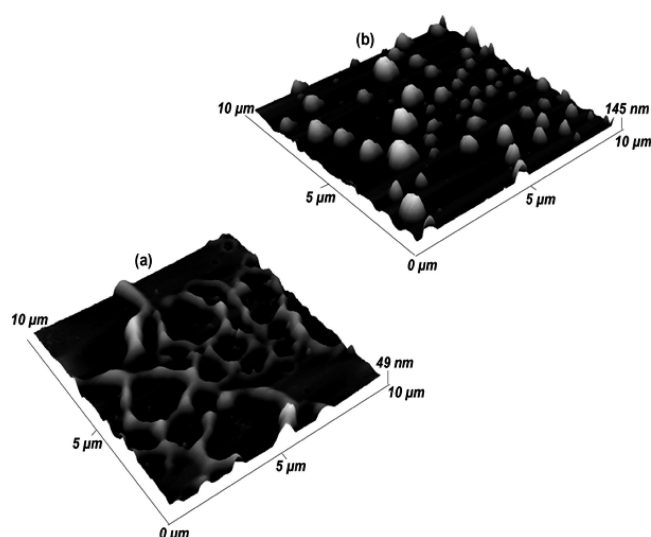


Figure 6. AFM micrographs of surface patterns formed by the TFPS(II) at 0.030 wt % (from toluene solution) on mica substrates (a) as pristine film (three-dimensional $10 \times 10 \mu\text{m}^2$ tapping-mode AFM scan) and (b) after thermal annealing at 200 °C for 30 min in air (three-dimensional $10 \times 10 \mu\text{m}^2$ tapping-mode AFM scan).

for 30 min in air, the morphology of the TFPS(I) as thin film at concentration 0.030 wt % from chloroform solutions exhibits the formation of isolated spheres (Figure 5c) of 250 nm in width. Therefore, the surface morphology of TFPS(I) after thermal

annealing exhibits the formation of isolated spheres regardless of the solvent used.

Finally, we have also examined the influence of the percentage of the rod portion to the organization of the copolymer. By keeping the solution concentration constant (0.030 wt %) and reducing the percentage of the terfluorene block in the copolymer (7.22% in the case of TFPS(II) vs 13.07% for TFPS(I)), we created interconnected elongated domains with dimensions of 1270 nm without the appearance of the spherical objects as in the case of TFPS(I) (Figure 6a). TFPS(II) after thermal treatment at 200 °C for 30 min in air exhibited the formation of spherical domains (Figure 6b) similar as in the case of TFPS(I) but with different dimensions (1030 nm in width).

4. Conclusions

The photophysical and morphological properties of a series of rod-coil diblock copolymers TFPS(I) and -(II) as pristine and annealed films were investigated by means of FT-IR, steady-state (cw-PL), time-resolved photoluminescence (TR-PL), and atomic force microscopy (AFM) techniques, respectively. On the basis of the results of the cw-PL technique on pristine and annealed films of TFPS(I) and -(II), an increase of the emission intensity after thermal treatment was observed. Furthermore, TR-PL studies on pristine and annealed films of TFPS(I) and -(II) clearly demonstrated an increase in the lifetime of the excited state due to the thermally induced ordered morphology of the film. This type of order was interpreted as a decrease of

structural defects after annealing. Finally, a clear change of the surface morphology of the block copolymers was observed after the application of thermal annealing based from the AFM measurements. Formation of well-defined spheres were observed for both the TFPS(I) and -(II) upon thermal treatment. Moreover, different morphologies were observed for TFPS(I) as thin films depending on the solvent used. However, after the same thermal processing both the different morphologies transformed to the formation of isolated spheres. Therefore, this class of block copolymer shows a great promise for the development of stable blue light emitting devices.

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