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Synthesis and Optical Properties on a Series of Polyethers Incorporating Terfluorene Segments and Methylene Spacers

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A series of polyethers consisting of a modified terfluorenediol connected with a nonconjugated spacer were synthesized and characterized in respect to their thermal, electrochemical, optical and morphological properties. The polymers were further investigated as thin deposits with the use of the FT-IR technique after thermal (200°C for 30 min) and photo-oxidation treatment. After thermal treatment no generation of the carbonyl stretching mode of the fluorenone moiety is observed, while after photo-oxidation in various times (between 5 to 30 min) the appearance of the fluorenone unit is well established. Furthermore, the length of the flexible spacer used influenced the optical properties of the polyethers after thermal treatment. In particular, odd ones showed more intensely the low energy emission band at 520 nm after the thermal treatment in contrast to even ones.

Keywords oligofluorenes, polyethers, conjugated polymers, AFM

Introduction

There is a great interest in developing efficient and stable polymeric blue light emitting diodes (PLEDs) in order to obtain the three primary colors. Many blue electroluminescent polymers have been synthesized, such as poly(*p*-phenylene)s (1), poly(vinylcarbazole)s (2), poly(oxadiazole)s (3), and poly(2,7-(9,9-dialkylfluorene))s (4), Among these polymers, poly(2,7-(9,9-dialkylfluorene))s (PFs) show particularly interesting optical and electrical properties for the development of blue light-emitting diodes. 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.

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Several attempts have been made to stabilize the blue color emission using either dendrimers (5) or bulky substituents (6) in the 9-position of the fluorene moiety, copolymerization techniques (7), oligomers (8), purification of the fluorene monomers before polymerization (9), and blends of polyfluorenes with some nonconjugated polymers such as polystyrene or poly(vinyl diphenylquinoline) (10), but the green electroluminescence band was not completely eliminated. The emission broad band at 520 nm has been attributed either to aggregation and/or excimer formation (11, 12) or to emission from fluorenone-like defects due to oxidative (photo- or electro) degradation of the film (13–15). However, a new hypothesis was recently made (16, 17), claiming that fluorenone alone is a necessary but not sufficient condition for the appearance of this undesirable low energy emission band at 520 nm. It was shown that inter-chain/inter-segment interactions are required for the appearance of the green emission band in the photoluminescence spectra of polyfluorenes.

Since high chemical purity and structural uniformity are considered as critical factors for PLED performance, monodispersed conjugated oligomers are used instead of conjugated polymers. However, oligomers are generally more prone to crystallization than polymers, resulting in polycrystalline films that scatter light and limit charge injection and transport. This observation combined with the necessity for processability in photonic polymers led some groups to the development of polymeric structures with repeating units consisting of a conjugated segment connected by a flexible nonconjugated spacer. Thus, a number of processable polymers emitting at various wavelengths have been synthesized and investigated (18–28).

In this work, we present the synthesis and characterization of a series of aromatic polyethers derived from terfluorene segments in respect to their thermal, electrochemical, optical and morphological properties. Moreover, particular interest was given to their optical properties after thermal annealing (200°C for 30 min in air) and photo-oxidation treatment.

Experimental

All the solvents and reagents were purchased from Aldrich and used without further purification unless otherwise stated. All reactions were run under inert atmosphere (argon). The modified terfluorenediol was synthesized based on a published procedure (29). Improvement of this procedure was achieved in the step of the synthesis of 2,7″-dibromo-9,9,9′,9′,9″,9″-hexahexyl-7,2′:7′,2″-terfluorene. The bromination reaction was carried out in chloroform for 2 h at 80°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.

The structures of the synthesized materials were clarified by ^{1}H and ^{13}C-NMR spectroscopy with a Bruker Avance DPX 400 and 100 MHz spectrometer, respectively. Gel permeation chromatography (GPC) measurements were carried out using a polymer lab chromatographer with two Ultra Styragel linear columns (10^4, 500 A), UV detector polystyrene standards and $CHCl_3$ as eluent, at 25°C with a flow rate of 1 mL/min. The absorption spectra were recorded on a Hewlett Packard 8452A Diode Array UV-Visible spectrophotometer. Fluorescence 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 photo-oxidation experiments, the samples were exposed in air and irradiated with UV light at 365 nm (~1000 mW) from an Efos Ultracure 100SS curing system. For the FT-IR and photoluminescence measurements thin films from chloroform solutions were spin-coated at a rotational speed of

2500 rpm and rotation duration time of 60 sec on barium fluoride (BaF_2) and quartz substrates, respectively. The absorbance intensity of the prepared thin films was adjusted below 0.1 in arbitrary units (in our case, all the thin films were at 0.07 a.u.) in order to ensure the same amount of the chromophore units in all the polyethers for the PL measurements. 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. Cyclic voltammetry (CV) studies were performed using a standard three-electrode cell. Platinum wires were used as counter and working electrodes. Silver/silver nitrate (0.1 M $AgNO_3$ in acetonitrile) was used as a reference electrode. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$; 98%) from Aldrich was used as electrolyte and was recrystallized three times from acetone and was dried in a vacuum at 100°C before each experiment. Ferrocene was provided from Aldrich and purified by sublimation before the experiments. Acetonitrile anhydrous 99.8% CH_3CN was also supplied from Aldrich and was used without further purification. All experiments were carried out in an air-sealed electrochemical cell. Before each experiment, the cell was purged with high-purity inert gas for 15 min. Before the start of the measurement, the inert gas was turned to "blanket mode". Measurements were recorded using a EG&G Princeton Applied Research potensiostat/galvanostat Model 263A connected to a personal computer running PowerSuite software. The scan rate was kept constant for all CV runs at 20 mV/s. The working electrode was cleaned before each experiment through sonication in 65% HNO_3, followed by subsequent sonication in absolute EtOH. The $Ag/AgNO_3$ electrode was connected to the electrochemical cell through a salt bridge and was calibrated before each experiment by running cyclic voltammetry on ferrocene. Imaging of the surface morphology of spin coated samples was accomplished via AFM. A Topometrix Explorer SPM Microscope (Theromicroscopes) with Electronic control unit ECU-Plus TM and Explorer SPM head with Truemetrix Scan Linearization having two dry scanners. Thin films from chloroform solutions of TF9 and TF10 were prepared as follows: 5 mg of the TF9 for example was dissolved in 1 mL chloroform 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 coated. The mica surface is atomically flat, which precludes any influence of the substrate topography on the observed morphology.

General Procedure for the Phase Transfer Polymerization Reaction

A mixture of aliphatic dibromide (0.1 mmol), terfluorenediol (0.1 mmol) and TBAH (0.04 mmol) was degassed three times before *o*-DCB (0.5 mL) and NaOH (10 N) (0.5 mL) were added. The mixture is vigorously stirred at 100°C for 5 days. Chloroform is then added, and the solution was filtered, precipitated into a 20-fold amount of methanol and dried under vacuum.

TF9

^{1}H-NMR ($CDCl_3$): $\delta = 7.8$ (m, 6H), 7.6 (m, 12H), 7.5 (d, 4H), 7.0 (d, 4H), 4.0 (t, 4H), 2.1 (broad, 12H), 1.8 (m, 4H), 1.4 (s, 8H), 1,25 (m, 2H), 1.1 (m, 38H), 0.7 (t, 32H). ^{13}C-NMR ($CDCl_3$): $\delta = 158.67$, 151.68, 140.54, 140.37, 139.97, 139.75, 139.45, 134.13, 128.13, 126.09, 125.58, 121.48, 121.11, 119.89, 114.87, 68.17, 55.24, 40.41, 31.43, 29.67, 29.50, 29.35, 26.07, 23.82, 22.52, 13.94.

TF10

^{1}H-NMR (CDCl$_3$): $\delta = 7.8$ (m, 6H), 7.6 (m, 12H), 7.5 (d, 4H), 7.0 (d, 4H), 4.0 (t, 4H), 2.1 (broad, 12H), 1.8 (m, 4H), 1.4 (s, 10H), 1.1 (m, 40H), 0.7 (t, 32H). ^{13}C-NMR (CDCl$_3$): $\delta = 158.68$, 151.68, 140.54, 140.37, 139.96, 139.74, 139.46, 134.11, 128.13, 126.11, 125.57, 121.46, 121.09, 119.92, 114.85, 68.19, 55.25, 40.41, 31.44, 29.68, 29.53, 29.38, 26.08, 23.84, 22.55, 13.95.

TF11

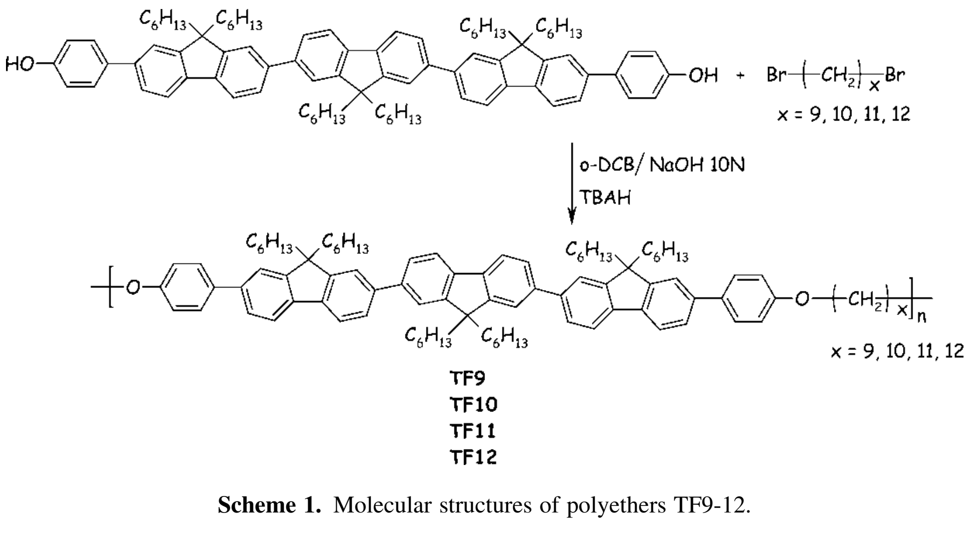
^{1}H-NMR (CDCl$_3$): $\delta = 7.8$ (m, 6H), 7.6 (m, 12H), 7.5 (d, 4H), 7.0 (d, 4H), 4.0 (t, 4H), 2.1 (broad, 12H), 1.8 (m, 6H), 1.3 (s, 12H), 1.1 (m, 40H), 0.7 (t, 30H). ^{13}C-NMR (CDCl$_3$): $\delta = 158.69$, 151.68, 140.54, 140.37, 140.09, 139.97, 139.75, 139.46, 134.10, 128.13, 126.10, 125.57, 121.47, 121.11, 119.91, 114.86, 68.20, 55.25, 40.41, 31.44, 29.67, 29.57, 29.41, 26.09, 23.82, 22.53, 13.96.

TF12

^{1}H-NMR (CDCl$_3$): $\delta = 7.8$ (m, 6H), 7.6 (m, 12H), 7.5 (d, 4H), 7.0 (d, 4H), 4.0 (t, 4H), 2.1 (broad, 12H), 1.8 (m, 4H), 1.5 (m, 4H), 1.3 (s, 14H), 1.1 (m, 38H), 0.7 (t, 30H). ^{13}C-NMR (CDCl$_3$): $\delta = 158.73$, 151.71, 140.57, 140.40, 140.13, 139.79, 139.50, 134.13, 128.17, 126.13, 125.61, 121.49, 121.15, 119.94, 114.89, 68.23, 55.28, 40.44, 31.47, 29.71, 29.63, 29.46, 29.38, 26.12, 23.85, 22.57, 13.99.

Results and Discussion

Polymerizations of the modified terfluorenediol with α,ω-aliphatic dibromides were conducted under phase transfer conditions in a mixture of *o*-DCB/NaOH (10 N) containing TBAH (*tert*-butylammoniumhydrogen sulfate) as the phase transfer catalyst (Scheme 1). Moreover, effort was devoted to accomplish the correct stoichiometries due to great differences between the monomers' molecular weights. Molecular weights



Scheme 1. Molecular structures of polyethers TF9-12.

Table 1
Molecular weight characteristics and glass transition temperature (T_g) of the synthesized polyethers

Polymers	Mn	Mw	PDI	T_g (°C)
TF9	18145	41290	2.27	67
TF10	24825	65865	2.65	66
TF11	13230	33860	2.56	67
TF12	34920	85160	2.44	61

between 13000 and 35000 were obtained for the synthesized polyethers (TF9-12) as determined by gel permeation chromatography (GPC) with polydispersities ranging from 2.27 to 2.65 (Table 1). Polyethers (TF9-12) were completely soluble in all chlorinated solvents at room temperature and were fully characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy, as can be viewed in Figure 1 for the case of TF11, with complete assignment of the peaks, proving the proposed structures.

Polyethers (TF9-12) were investigated for their thermal and electrochemical properties through differential scanning calorimetry (DSC; Table 1) and cyclic voltammetry techniques, respectively. The glass transition temperature (T_g) of the polyethers TF9-11

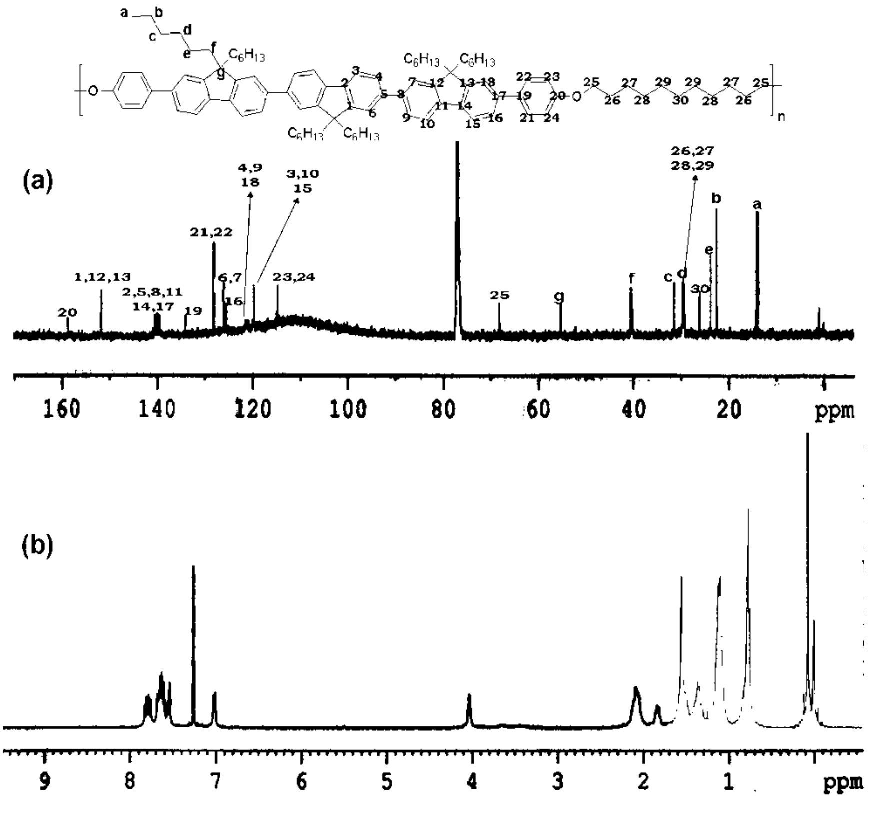


Figure 1. (a) ^{13}C-NMR and (b) ^{1}H-NMR of polyether TF11.

is typically the same (66–67°C), while TF12 shows a T_g at 61°C. These values are in agreement with other polymers reported in the literature consisting of oligofluorene segments (30). Moreover, the synthesized polyethers are amorphous based on the results of the DSC thermograms. This particular property is desirable in cases where these materials will be used in the preparation of electronic devices in order to prevent crystallization in these devices. In an effort to determine the HOMO and LUMO energy levels of the polyethers, cyclic voltammetry was employed for the case of TF11 in thin film form. The potential values obtained vs. Ag/Ag^+ were converted vs. saturated calomel electrode (SCE). The energy levels were calculated using the following empirical equation (31): $\text{HOMO} = 4.4 + (E^{ox}_{onset})$ and $\text{LUMO} = 4.4 + (E^{red}_{onset})$. From the cyclic voltammogram in Figure 2, the oxidation peak at 1.01 V with an onset at 0.84 V gives a HOMO energy value of 5.24 eV. The reduction peak at −2.20 V (onset −2.14 V) gives a LUMO energy level of 2.26 eV. The electrochemical band gap, determined by the oxidation and reduction onsets, was calculated 2.98 eV, which is in a good agreement with the optical band gap (as calculated from the onset of the absorption spectra in thin film) of 3.0 eV.

The FT-IR spectra of the thermally and photo-oxidative treated polyethers TF9-12 as thin films are presented in Figures 3 and 4. The thermal treatment of polyethers at 200°C for 30 min in air reveals no generation of the 1726 cm^{-1} band (see Figure 3 for polymer TF11 as an example) assigned to the carbonyl stretching mode of the fluorenone moiety (32). Additionally, the FT-IR spectra of the photo-oxidative treated polyethers TF9-12 as thin films are presented in Figure 4. The insets of Figure 4 represent the 1850–1650 cm^{-1} region spectra of polyethers TF9-12 and indicate the progressive increase of the 1726 cm^{-1} band upon UV treatment in the different periods of time (5, 15, and 30 min) for all the studied materials. Furthermore, a new band at 1775 cm^{-1} is present as a shoulder and these features suggest that upon degradation, except from the fluorenone moieties, another type of chemical species is also created.

UV-VIS absorption spectra of polyethers TF9-12 in a chloroform solution are shown in the inset of Figure 5a. An absorption maximum at 364 nm due to the π-π^* transition of the terfluorene segments is observed for all polyethers. Passing from solution to the solid state, the absorption maxima of all polyethers remains unchanged. The photoluminescence spectra of the studied materials in chloroform solution are depicted in Figure 5a. In all cases, vibronic peaks at 412, 431 and 466 nm are observed, assigned to the 0-0, 0-1 and

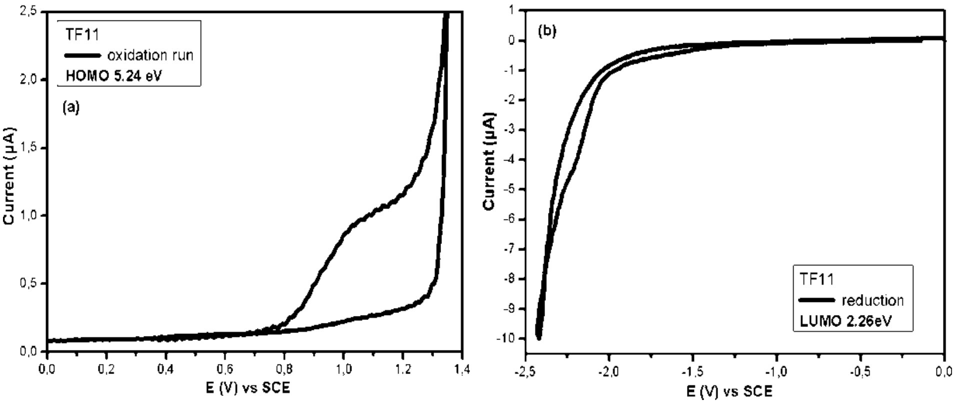


Figure 2. Cyclic voltammetry of polyether TF11 in thin film. Scan rate, 20 mV/s.

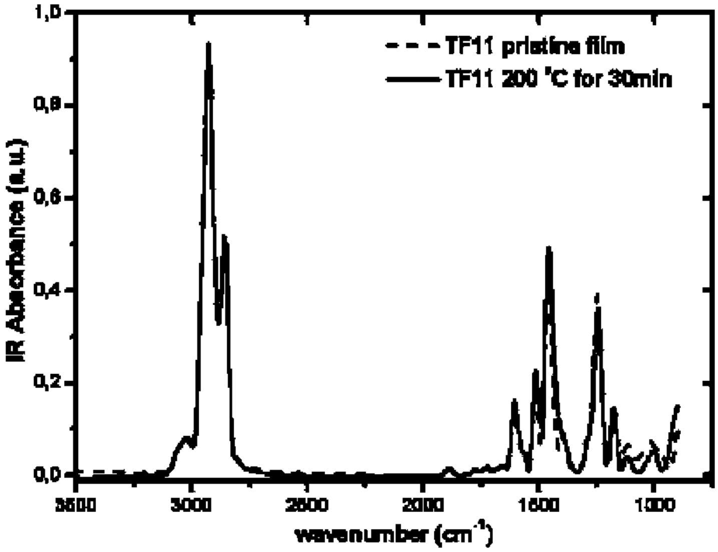


Figure 3. FT-IR spectra of TF11 as pristine film and after annealing at 200 °C for 30 min in air.

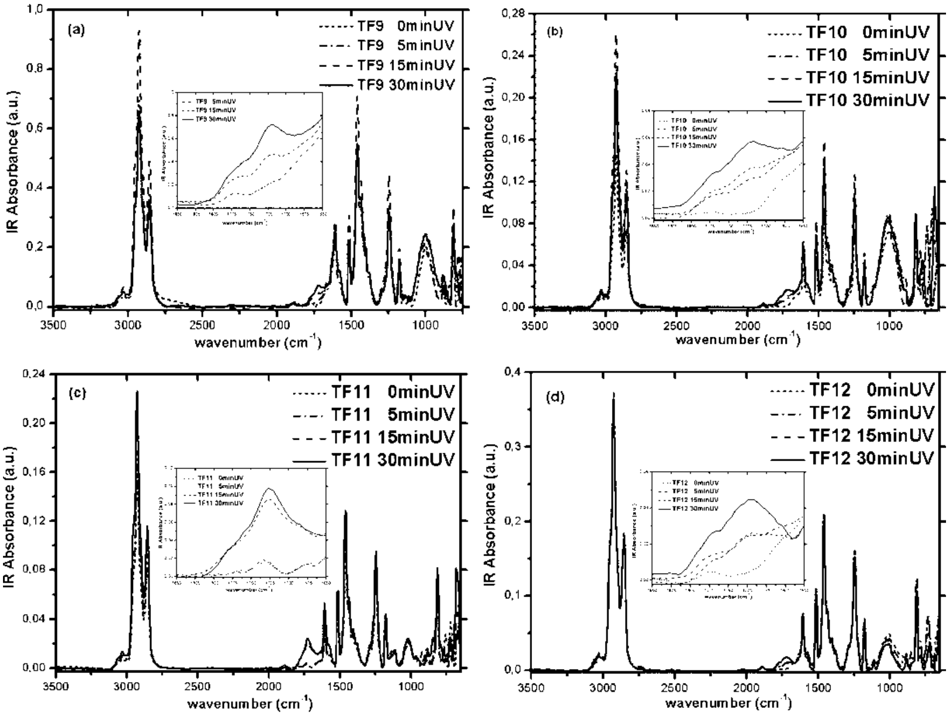


Figure 4. FT-IR spectra of (a) TF9, (b) TF10, (c) TF11 and (d) TF12 as pristine films and after UV treatment in air (exposure for different periods of times between 5 and 30 min).

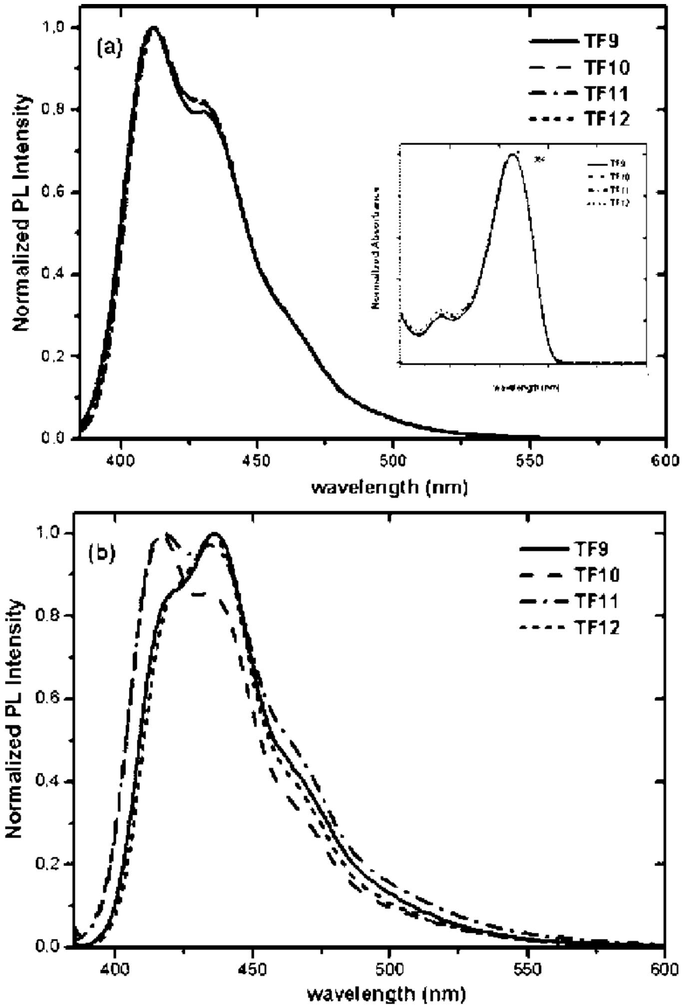


Figure 5. Photoluminescence spectra of TF9-12 (a) in chloroform solution and (b) in the solid state. Excitation wavelength was 360 nm. In the inset, the UV-Vis absorption spectra of TF9-12 in chloroform solution are presented.

0-2 intra-chain singlet transitions, with the 0-0 transition being the most intense. In the solid state (Figure 5b), the emission spectra of the polyethers were red shifted by 4 nm (emission maxima at 416, 435, and 470 nm) showing an increase of the planarity of the polyethers in the solid state. Moreover, the 0-1 intra-chain singlet transition became the most intense for the case of TF9 and TF12 and also no emission band at 520–530 nm is observed for all the materials.

In order to investigate the influence of the thermal treatment on the optical properties of the synthesized materials, we studied the photoluminescence spectra of TF9-12 as thin films after annealing in air at 200°C for 30 min (Figure 6). It is clearly observed that in all polyethers the low energy emission band at 520 nm is present after thermal treatment. Therefore, since the fluorenone moiety (one of the reasons for the appearance of the low-energy green emission band as it was mentioned in the

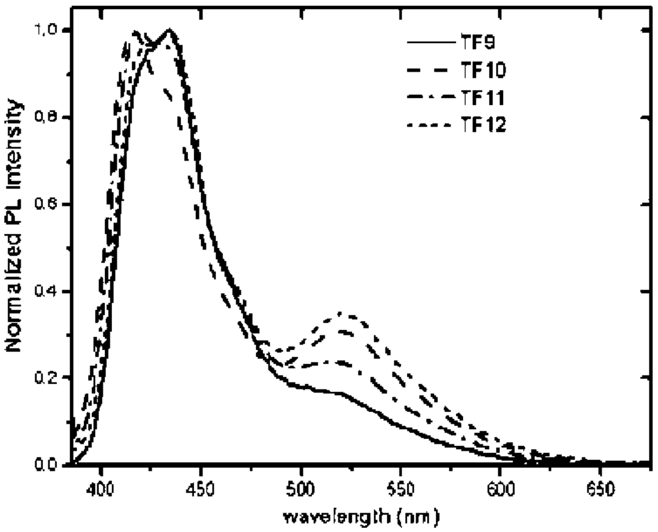


Figure 6. Photoluminescence spectra of polyethers TF9-12 in the solid state upon thermal annealing (200°C for 30 min) in air.

introduction) is not generated upon annealing of the terfluorene segments (Figure 3), then any observed difference on the optical properties of the polyethers TF9-12 can safely be attributed to the increment of the inter-segment interactions of the terfluorene blocks upon annealing in the solid state. Moreover, the emission spectra of the polyethers after thermal treatment were influenced from the length of the flexible spacer used. Polyethers TF10 and TF12 (odd methylene spacers) showed a larger increase of the emission band at 520 nm in contrast to polyethers TF9 and TF11 (even methylene spacers) (Figure 6) which support the view that the inter-segment interactions between the terfluorene blocks are responsible for the observed behavior.

The results of the investigation of the influence of the photo-oxidation under diffuse UV radiation at ambient atmosphere on the optical properties of the studied materials are presented in Figure 7. The emission spectrum in arbitrary units of the TF9 (Figure 7a) after photo-oxidation in various times (5, 15, and 30 min) is subsequently quenched because the fluorenone moieties which are created (Figure 4a) upon this treatment are efficient exciton traps. In addition, the normalized emission spectrum of TF9 after photo-oxidation in various times (Figure 7a) reveals the subsequent appearance of the 520 nm emission band. Similar results are presented for the case of TF10, TF11 and TF12 upon the same photo-oxidation treatment (Figures 7b–d).

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 photo physical properties with the sample morphology of the studied polyethers. Thus, surface patterns of TF9 and TF10 as thin deposits and after annealing in conditions similar to those reported for the FT-IR and photoluminescence techniques were observed using the AFM technique (Figures 8 and 9). Irregular structures are obtained for TF9, while a fine structure with nanometer separation in 105 nm was observed for the case of TF10 (Figures 8a–9a), which do not influence the color purity of the polymers (no appearance of the low energy emission band as shown in Figure 5b). After thermal annealing at

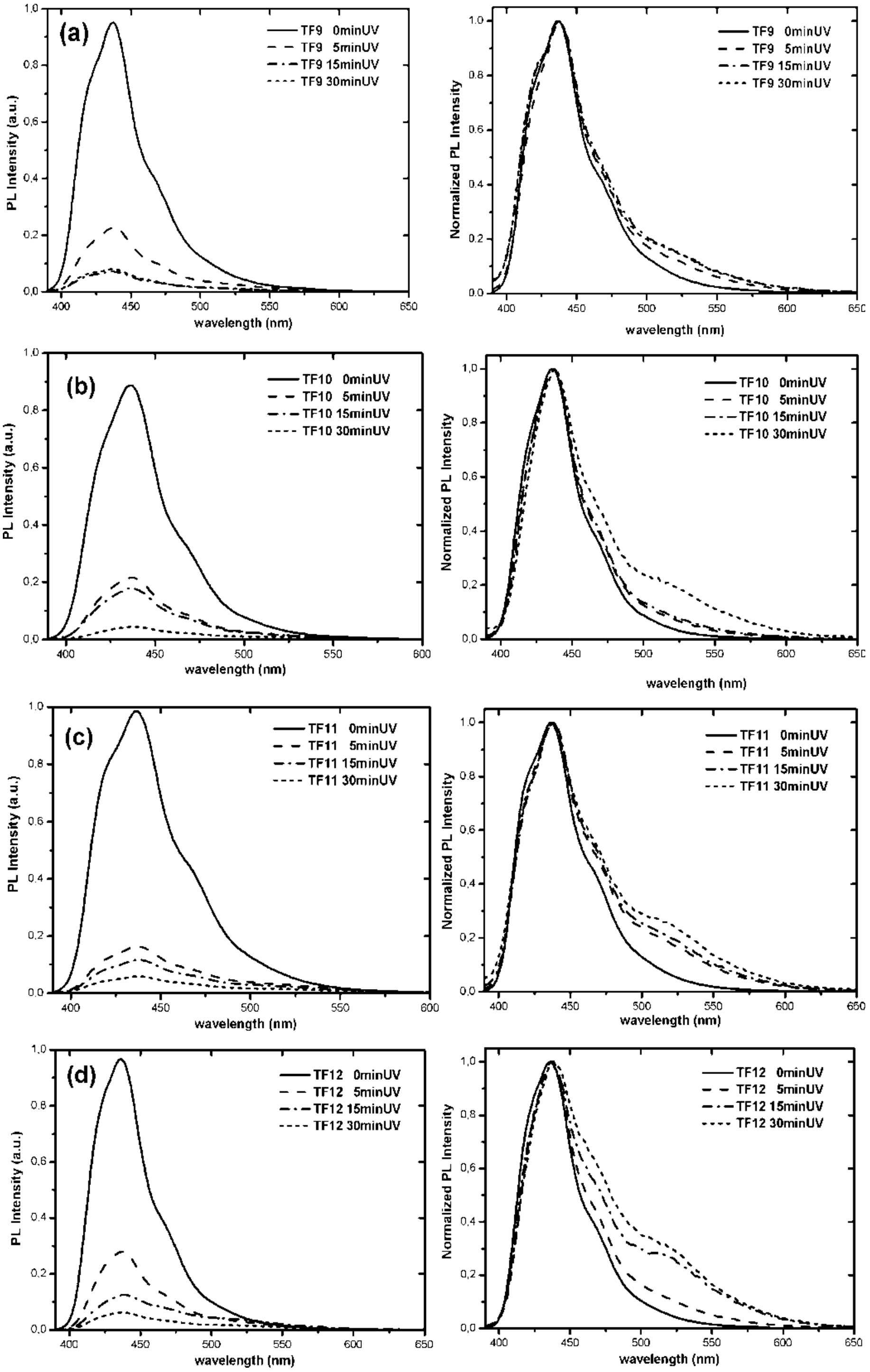


Figure 7. Photoluminescence spectra in arbitrary units and normalized of (a) TF9, (b) TF10, (c) TF11 and, (d) TF12 as pristine films and after UV treatment in air (exposure for different periods of times between 5 and 30 min).

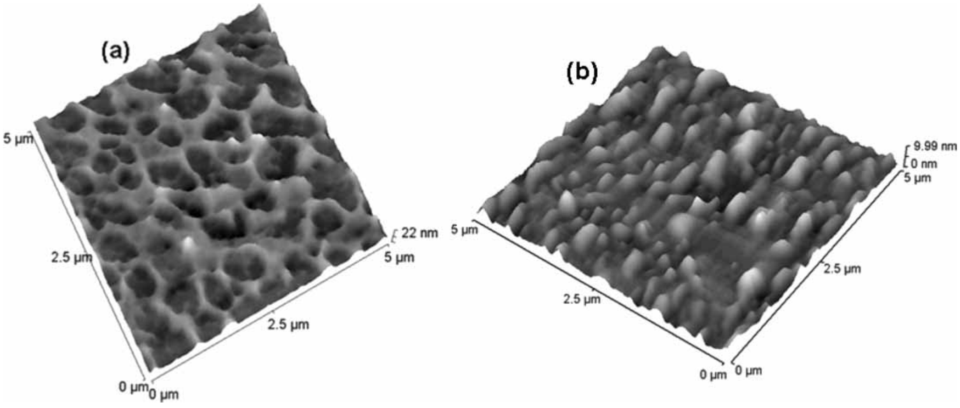


Figure 8. AFM micrographs of TF9 as pristine film and after annealing at 200°C for 30 min (Three dimensional 5 × 5 µm tapping-mode AFM scan).

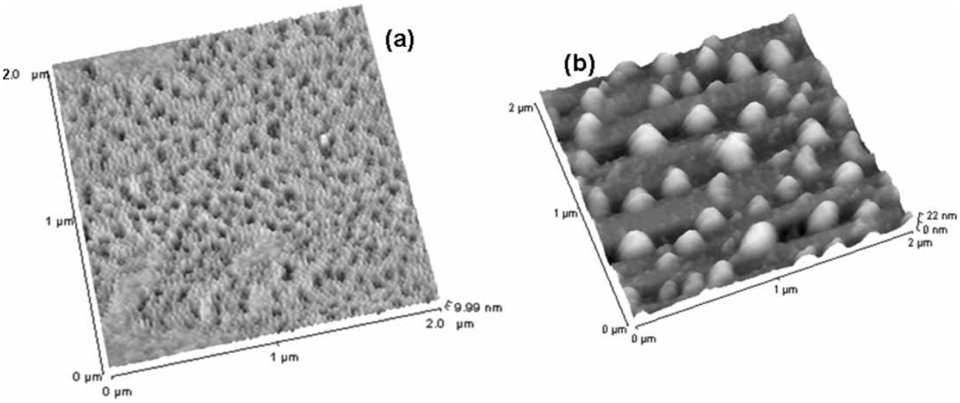


Figure 9. AFM micrographs of TF10 as pristine film and after annealing at 200°C for 30 min (three dimensional 2 × 2 µm tapping-mode AFM scan).

200°C for 30 min in air, a clear change of the surface morphology of TF9 and TF10 is observed (Figures 8b–9b) which manipulates the optical properties of the polyethers (Figure 6). In particular, spherical domains with dimensions of 426 nm and 230 nm in width and 10 nm and 22 nm in height for the case of TF9 and TF10 respectively, were appeared.

Conclusions

Polyethers consisting of terfluorene segments and different methylene spacers were synthesized resulting in soluble, easily processable and amorphous polymeric materials. All the studied materials were investigated using the FT-IR technique after thermal and photo-oxidation treatment. Thermal annealing in air at 200°C for 30 min reveals no generation of the fluorenone unit in contrast to photo-oxidation treatment where the creation of the carbonyl stretching mode of the fluorenone moiety is well documented. Moreover, all polymers were studied with respect to their optical properties before and after thermal and photo-oxidation treatment. All polyethers emit pure blue light as pristine films while after the thermal and photo-oxidation treatment the blue light is converted to an undesirable blue-green shade with the appearance of the low energy emission band at 520 nm, which is influenced from the length of the aliphatic spacer. Odd methylene spacers showed more intense the low energy emission band at 520 nm after thermal annealing in contrast to even ones. Finally, morphological characterization of TF9 and TF10 was performed using the AFM technique.

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