Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Random Copolymers Combining Terfluorene Segments and Hole or Electron Transporting Moieties

Christos L. Chochos[ab]; Nikos P. Tzanetos[ab]; Solon P. Economopoulos[ab]; Vasilis G. Gregoriou[b]; Joannis K. Kallitsis[ab]
[a] Department of Chemistry, University of Patras, Patras, Greece [b] Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT), Patras, Greece

To cite this Article Chochos, Christos L. , Tzanetos, Nikos P. , Economopoulos, Solon P. , Gregoriou, Vasilis G. and Kallitsis, Joannis K.(2007) 'Synthesis and Characterization of Random Copolymers Combining Terfluorene Segments and Hole or Electron Transporting Moieties', Journal of Macromolecular Science, Part A, 44: 9, 923 — 930

To link to this Article: DOI: 10.1080/10601320701424172

URL: http://dx.doi.org/10.1080/10601320701424172

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 923–930

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701424172

Synthesis and Characterization of Random Copolymers Combining Terfluorene Segments and Hole or Electron Transporting Moieties

CHRISTOS L. CHOCHOS,[1,2] NIKOS P. TZANETOS,[1,2] SOLON P. ECONOMOPOULOS,[1,2] VASILIS G. GREGORIOU,[2] and JOANNIS K. KALLITSIS[1,2]

[1]*Department of Chemistry, University of Patras, Patras, Greece*
[2]*Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT), Patras, Greece*

Received and accepted February, 2007

New random copolymers having a well defined terfluorene unit with different hole or electron transporting moieties such as vinyl-carbazole (scTFPCARBZ) and side chain oxadiazole (scTFPOXD) were synthesized using the free radical polymerization technique. The synthesized materials were characterized with a variety of spectroscopic techniques such as ^{1}H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), cyclic voltammetry, Fourier transform infrared spectroscopy, UV-Vis absorption and photoluminescence. All the copolymers exhibit blue light emission, while an efficient energy transfer was detected from the oxadiazole-based homopolymer to the terfluorene block both in solution and in the solid state for scTFPOXD. Finally, the influence of the photo-oxidation treatment on the optical properties of the random copolymers was examined.

Keywords: polyfluorenes; oligofluorenes; conjugated polymers; random copolymers; FT-IR

1 Introduction

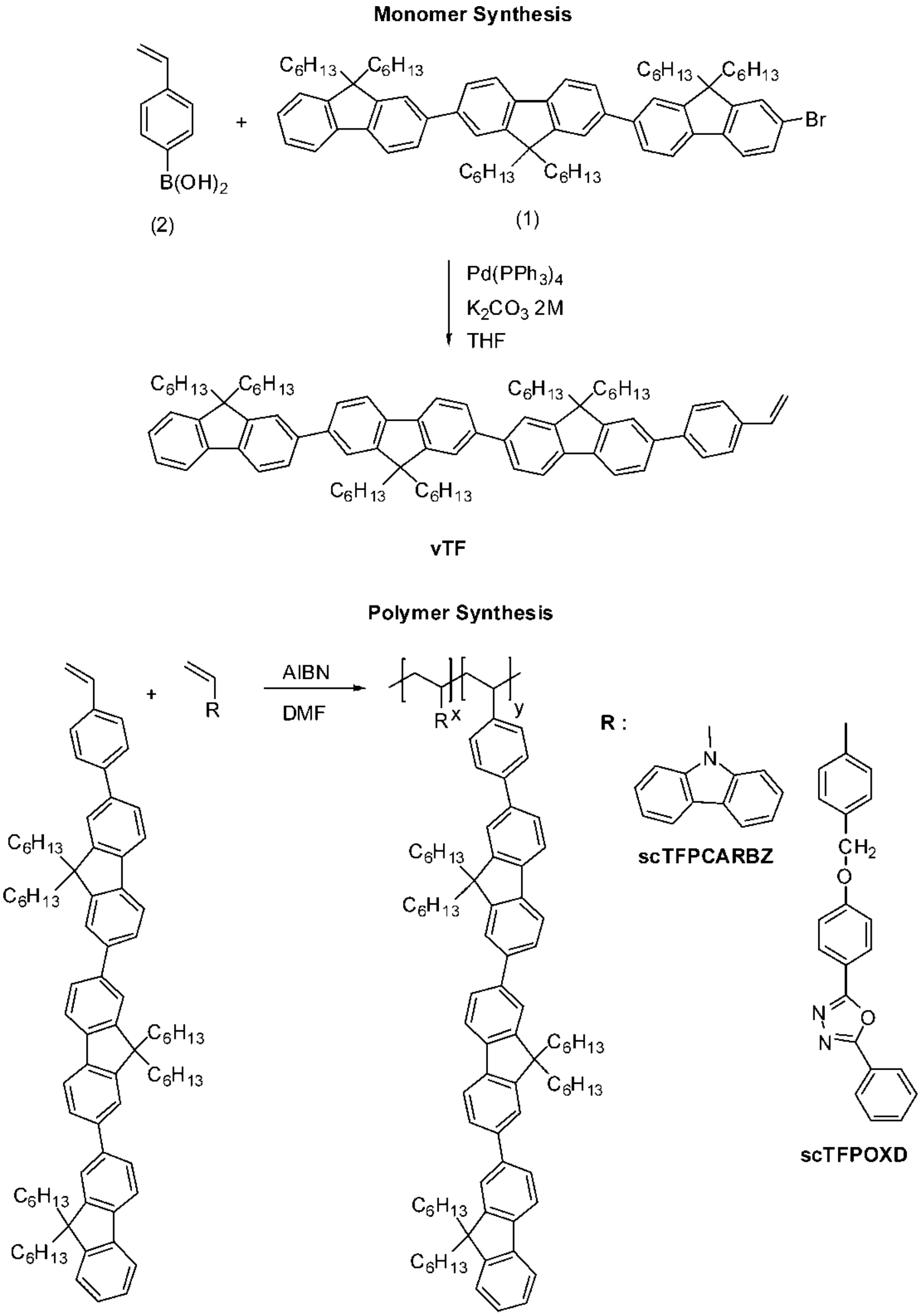
Polyfluorenes (PFs) (1–3) have emerged as an attractive class of electroluminescent conjugated polymers for use in polymer light emitting diodes as blue emitters, exhibiting high photoluminescence quantum yields in the solid state. However, the major disadvantage of PF-based LEDs is their poor spectral stability under normal operation with the appearance of a low-energy emission band occurring at 520–530 nm (4). Until now, the origin of this band remains a matter of debate in the literature (5–16). Other key issues, such as the long-term stability, color purity and tunability as well as balanced charge mobilities should be resolved for the commercialization of PLEDs. Thus, the design of new materials which will overcome the current problems as the restricted charge mobility and the color degradation is very important.

In order to achieve controlled charge mobility, combination of oligofluorenes or polyfluorenes with hole or electron transporting units in a copolymer structure has been studied. Polymers containing oxadiazole derivatives either in the main chain or side chains have been widely used as electron transporting/hole blocking materials in organic LEDs, while carbazole-based conjugated polymers have demonstrated strong hole-transporting ability in optoelectronic devices (17, 18). Both carbazole- and oxadiazole-based electroluminescent polymers demonstrate quite different charge injection and transporting abilities for holes and electrons in polymer light-emitting diode (PLED) devices. One approach for the improvement of the balanced charge injection is the combination of a carbazole moiety (a typical hole transporting unit) or an oxadiazole unit (an electron transporting unit) into the same polymer backbone either in the main chain or as side chain pendants with the conjugated polymer or oligomer that serve as the emissive layer (19–23).

In this report, we have prepared a series of novel random copolymers having a well-defined terfluorene unit with different hole or electron transporting moieties, such as side chain oxadiazole (scTFPOXD) and side chain carbazole (scTFPCARBZ), using the free radical polymerization

---

Address correspondence to: Joannis K. Kallitsis, Department of Chemistry, University of Patras, Patras 26500, Greece and Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT), P. O. Box 1414, Patras 26500, Greece. E-mail: j.kallitsis@chemistry.upatras.gr



Sch. 1. Molecular structures of the vinyl-terfluorene molecule vTF, scTFPOXD, and scTFPCARBZ copolymers.

technique (Scheme 1). The chemical structures of the copolymers were clarified by ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC) (Figure 1). The synthesized copolymers were further characterized with a variety of spectroscopic techniques such as differential scanning calorimetry (DSC), cyclic voltammetry, UV-Vis and photoluminescence (PL). Finally, a combination of FT-IR measurements on thin polymer films after photo-oxidation treatment in air with the subsequent collection of the photoluminescence spectra were used in order to examine any observed differences in the chemical structure and the optical stability of the copolymers.

2 Experimental

2.1 Instrumentation and Measurements

The synthesized monomers and polymers were characterized using ^{1}H and ^{13}C-NMR spectroscopy with a Bruker Avance

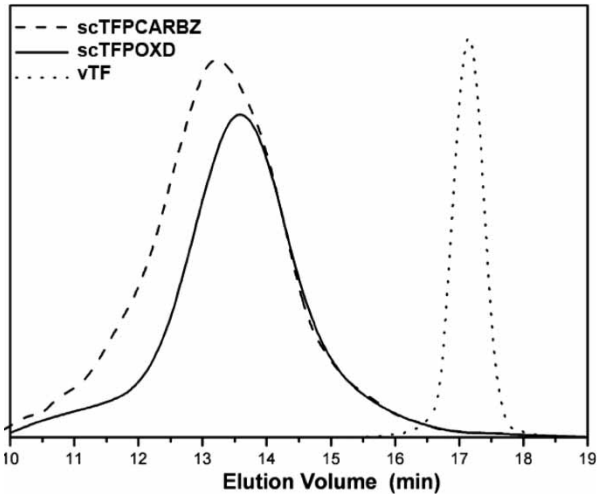


Fig. 1. GPC chromatograms of scTFPOXD, scTFPCARBZ, and vTF.

DPX 400 and 100 MHz spectrometer, respectively. The obtained molecular weights were estimated by gel permeation chromatography (GPC) using a polymer lab chromatographer equipped with two Ultra Styragel linear columns (10^4, 500 A), UV detector. Calibration was made using polystyrene standards and $CHCl_3$ as eluent, at 25°C with a flow rate of 1 mL/min. The UV spectra were recorded on a Hewlett Packard 8452A Diode Array UV-Visible spectrophotometer. Fluorescence was measured on a Perkin-Elmer LS45 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. 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 an electrolyte and recrystallized three times from acetone and dried in a vacuum at 100°C before each experiment. Ferrocene was provided from Aldrich and was purified by sublimation before the experiments. Acetonitrile anhydrous 99.8% CH_3CN was also supplied from Aldrich and 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.

2.2 Monomer and Polymer Synthesis

All the solvents and reagents were purchased from Aldrich and used without further purification unless otherwise stated. The vinyl-oxadiazole (24, 25) (monomer (I)) was prepared according to literature procedures, while 9-vinylcarbazole (monomer (II)) was recrystallized from methanol before use. All reactions were run under inert atmosphere (argon) and DMF was purged with argon for 1 h before use.

2.3 Synthesis of the Vinyl-Terfluorene Monomer (vTF)

Under an argon atmosphere, 4-styrylboronic acid (1) (0.222 g, 1.5 mmol), 2-bromo-9,9,9′,9′,9″,9″-hexahexyl-7,2′:7′,2″-terfluorene (2) (1.077 g, 1 mmol), $Pd(PPh_3)_4$ (86.6 mg, 0.075 mmol), THF (20 mL) and 2 M K_2CO_3 (3.75 mmol, 1.875 mL) were placed in a one-necked flask and refluxed for 72 h. After cooling, the mixture was precipitated into methanol (20 fold excess of volume) and the solid precipitate formed was filtrated and diluted with acetone (20 mL). The solution was precipitated in hexane (80 mL) and the white solid formed was filtrated, collected and dried under vacuum at room temperature. Yield 64%, 0.704 g.

2.3.1 vTF

^{1}H-NMR ($CDCl_3$): $\delta = 7.74$–7.80 (m, 6H), 7.52–7.67 (m, 14H), 7.36 (m, 3H), 6.80 (q, 1H), 5.80 (d, 1H), 5.28 (d, 1H), 2.09 (broad, 12H), 1.09 (m, 36H), 0.77 (t, 30H).

^{13}C-NMR ($CDCl_3$): $\delta = 151.80$, 151.49, 151.03, 141.12, 140.82, 140.52, 140.34, 140.21, 139.97, 139.55, 136.49, 127.27, 126.99, 126.80, 126.68, 126.16, 126.04, 125.90, 122.94, 121.52, 121.38, 119.99, 119.19, 113.80, 55.32, 55.18, 40.92, 31.46, 29.69, 23.84, 22.56, 14.00.

2.3.2 Free-Radical Copolymerization of the vTF with the Monomers I or II

A solution of the vinyl terfluorene monomer vTF (113.8 mg, 0.103 mmol), monomer (I) (329.8 mg, 0.931 mmol) or monomer (II) (180 mg, 0.931 mmol) and AIBN (2.5% mol of monomers) in dry DMF (3 mL) was degassed three times and flushed with argon. The mixture was heated under stirring in a sealed tube for 3 days. After cooling to room temperature, $CHCl_3$ (10 mL) was added to the reaction mixtures in order to dissolve the copolymers. The copolymers were precipitated in a large excess of methanol (20-fold excess by volume) and further purified by reprecipitation from $CHCl_3$ into ethyl acetate. Thus, the obtained white solids were dried under vacuum at room temperature.

3 Results and Discussion

3.1 Monomer and Polymer Synthesis

Among the various techniques to polymerize vinyl monomers, the most widely used technique still remains the technique of free radical polymerization. This technique requires mild reaction conditions and is suitable for a wide range of functional monomers. Free radical polymerization with AIBN as the initiator was utilized for the copolymerization of the new vinyl terfluorene monomer vTF with the monomers vinyl-carbazole or vinyl-oxadiazole. For the preparation of the vinyl-terfluorene monomer (vTF) (Scheme 1), a palladium-mediated Suzuki coupling reaction (26) was performed between the 2-bromo-9,9,9′,9′,9″,9″-hexahexyl-7,2′:7′,2″-terfluorene (1) and the vinyl-phenylboronic acid (2). The ^{1}H-NMR spectra of vTF is depicted in Figure 2a. Unfortunately, homopolymerization of vTF gave an insoluble product. Therefore, copolymerization of vTF in a percentage of ~10% was carried out with the monomers (I) and (II). In the case of the soluble copolymers, the unreacted monomers were effectively removed using dissolution of the reaction mixture and precipitation in a good solvent for the above substances (ethyl acetate for the monomers I and II). The resulting copolymers scTFPOXD and scTFPCARBZ exhibited good solubility in $CHCl_3$. Gel permeation chromatography was used in order to make sure that no trace of unreacted monomers remained in the obtained copolymers. The homogeneity of the copolymers was also assessed by gel permeation chromatography based on calibration with polystyrene standards, revealing a M_n of 18000 and 21070

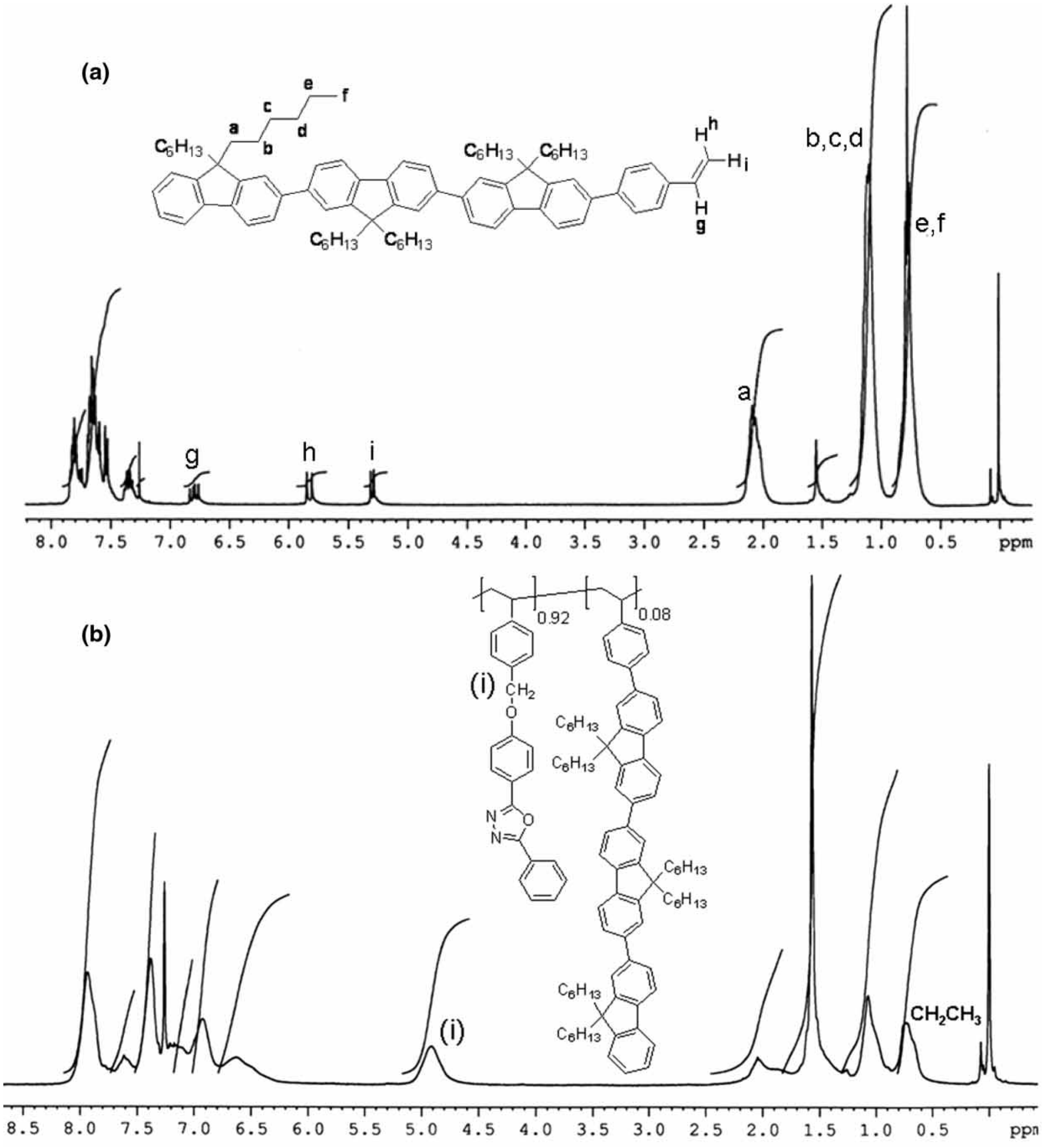


Fig. 2. ^{1}H-NMR spectra of (a) vTF and (b) scTFPOXD in $CDCl_3$ at room temperature.

and polydispersity indices (M_w/M_n) of 1.52 and 1.98 for scTFPOXD and scTFPCARBZ, respectively, (Figure 1). The characterization data of the two different copolymers are summarized in Table 1. From the ^{1}H-NMR spectra of the copolymer scTFPOXD (Figure 2b) we can calculate the terfluorene content in the copolymer, based on the aliphatic -CH_2CH_3 protons at $\delta = 0.73$ ppm of vTF and the signal at $\delta = 5.00$ ppm corresponding to methylene protons in the α-position to the oxygen of the oxadiazole monomer I. In the case of scTFPCARBZ, the calculation for the terfluorene content was based on the aliphatic -CH_2CH_3 protons at $\delta = 0.73$ ppm of vTF and the signal at 5.00 ppm corresponding to -CH proton in the vinyl-position of the carbazole monomer II. The calculated terfluorene content is 8% in scTFPOXD and 6% in scTFPCARBZ.

3.2 Thermal and Electrochemical Properties

The thermal properties of the random copolymers scTFPOXD and scTFPCZ were examined using differential scanning calorimetry (DSC) and their T_g's appeared at 124°C and 222°C, respectively (Table 1). In addition, the random copolymers resulted in DSC traces that show no crystallizing and melting peaks, but only glass transition temperatures which mean that the random 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.

Cyclic voltammetry (CV) was used to assess the ionization potentials (E_{HOMO}) and the electron affinity (E_{LUMO}) of the random copolymers. The potential values obtained vs. Ag/Ag^+ were converted vs. saturated calomel electrode (SCE). The energy levels were calculated using the following empirical equation: (27–29) $HOMO = 4.4 + (E^{ox}_{onset})$ and $LUMO = 4.4 + (E^{red}_{onset})$, where the E^{ox}_{onset} and E^{red}_{onset} are the onset oxidation potential and the onset reduction potential vs. SCE, respectively. The calculated energy levels for all studied materials are presented in Table 1. The scTFPOXD exhibited irreversible characteristics (oxidation, reduction; Figure 3a) and energy levels lying at 5.5 eV (E_{HOMO}) and 2.5 eV (E_{LUMO}). The scTFPCARBZ displayed only an irreversible oxidation (Figure 3b) and the energy levels were estimated at 5.4 eV (E_{HOMO}) and 2.4 eV (E_{LUMO}). The electrochemical band gap determined by the oxidation and reduction onsets of the scTFPOXD was in very good agreement with the optical band gap as calculated from the onset of the absorption spectra in thin film form (Table 1). In the case of scTFPCARBZ, the E_{LUMO} was calculated from the E_{HOMO} minus the optical band gap E_g(opt) as calculated from the onset of the absorption spectra.

Table 1. Reaction condition, molecular weight characteristics, glass transition temperatures and the energy levels of the synthecsized copolymers

Polymers	M_n (GPC)	PDI	T_g (°C)	E_{HOMO}, E_{LUMO} (eV vs vacuum)	E_g(opt.)[b], E_g(CV)[c] (eV)
scTFPOXD[a]	18000	1.52	124	5.5, 2.5	2.96, 3.0
scTFPCARBZ	21070	1.98	222	5.4, 2,4	2.98, —

[a] Reaction conditions: AIBN, DMF, 110°C.

[b] E_g(opt.): Optical band gaps as calculated from the onset of the absorption spectra of the copolymers in thin film form.

[c] E_g(CV): Electrochemical band gaps determined using $E_{HOMO}-E_{LUMO}$.

3.3 Spectroscopic Characterization using FT-IR Spectroscopy

In order to evaluate the impact of the photo-oxidation treatment on the chemical structure of the studied materials, thin deposits were studied using the FT-IR spectroscopy. The FT-IR spectra of the photo-oxidative treated scTFPOXD and scTFPCARBZ as thin films in the 1850–1700 cm^{-1} region are presented in Figure 4. The spectra of the studied materials are dominated by the appearance of the 1726 cm^{-1} band after 30 min under UV exposure which is

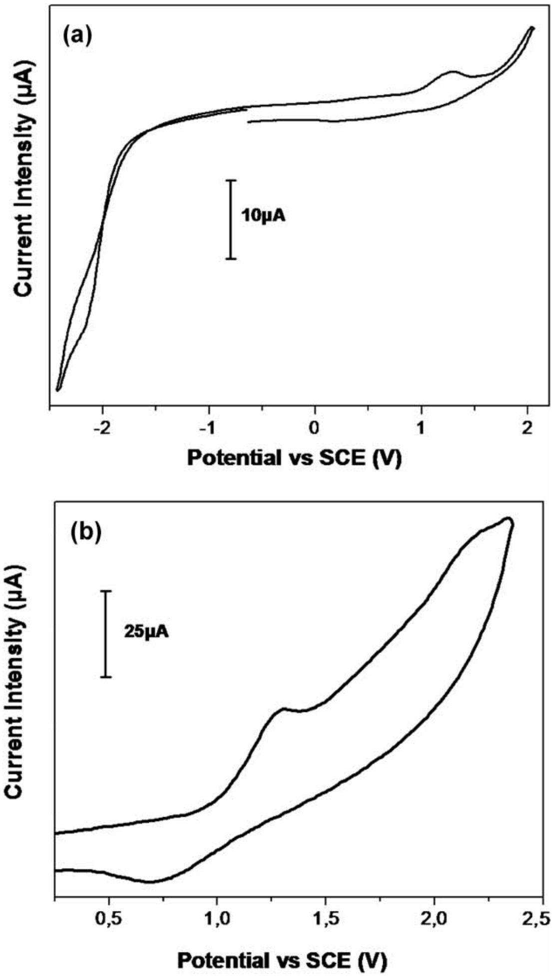


Fig. 3. CV curves of the (a) scTFPOXD and (b) scTFPCARBZ as thin films.

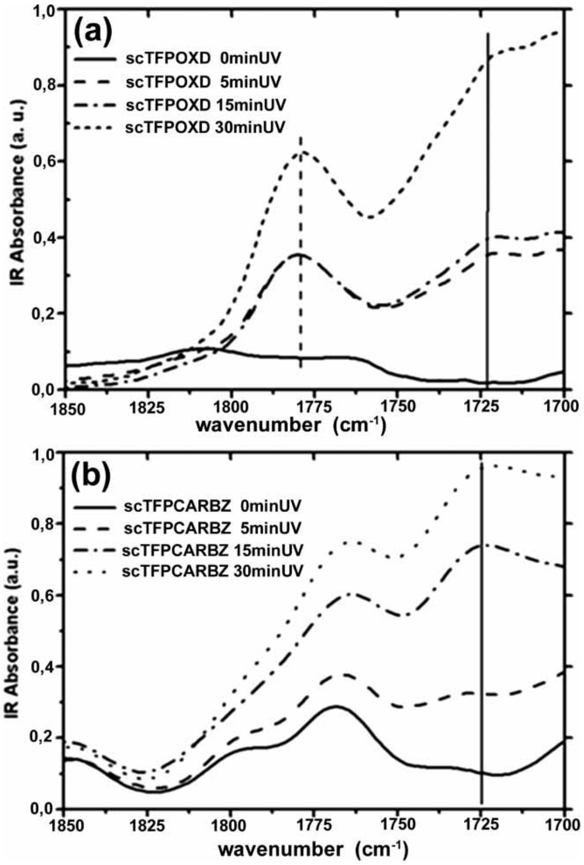


Fig. 4. FT-IR spectra of (a) scTFPOXD and (b) scTFPCARBZ as pristine films and after UV treatment in air (exposure for different periods of times between 5 and 30 min).

assigned to the carbonyl stretching mode of the fluorenone moiety (30). Furthermore, it is obvious the progressive increase of the 1726 cm^{-1} band under UV treatment in the different time periods (5, 15, and 30 min) for scTFPOXD and scTFPCARBZ (Figures 4a–b). In addition, a new band located near to 1775 cm^{-1} is present as a shoulder, and these features suggest that upon degradation except from the fluorenone moieties, some other type of chemical species are also created, as was also observed by other groups, (31, 32) which only recently have been identified (33).

3.4 Optical Properties

The UV-Vis absorption data of the scTFPOXD and scTFPCARBZ in chloroform solutions and in solid state are summarized in Table 2. The absorption spectrum of the scTFPOXD is a sum of the optical properties of the terfluorene segment and the oxadiazole homopolymer, respectively. The absorption maximum of the oxadiazole-based part in scTFPOXD is at 294 nm in solution and 298 nm in the solid state similar to those reported in previous work, (24, 25) while the π-π^* transition of the terfluorene segment is at 360 nm in solution and at 370 nm in the solid state (34, 35). In the case of scTFPCARBZ, only one absorption band is observed at 350 nm both in solution and in solid state because the absorption maximum of the carbazole homopolymer located at 345 nm, both in solution and in solid state (36, 37), is overlapped from the absorption band of the terfluorene segment.

The photoluminescence spectra of the studied materials in chloroform solution and in solid state are depicted in Figure 5 and the results are summarized in Table 2. All the materials display a progression of vibronic peaks assigned to the 0–0, 0–1, and 0–2 intra-chain singlet transitions in solution similar to those of the polyfluorenes when the excitation wavelength is at the absorption maxima of the terfluorene moiety. On the contrary, while scTFPCARBZ exhibits the same progression of vibronic peaks in the emission spectra in the solid state as in solution (excitation wavelength at the absorption maxima of the terfluorene moiety), the vibronic features of scTFPOXD became less resolved because only two electronic transitions at 430 and 466 nm were presented in the solid state, respectively.

An efficient energy transfer from the poly(oxadiazole) based segment to the terfluorene rigid unit occurs when the excitation wavelength is at the absorption maxima of the oxadiazole-based part in scTFPOXD, both in solution and in solid state (Figure 6), and the copolymer emits pure blue light from the terfluorene unit regardless of the excitation wavelength. The origin of this energy transfer can be attributed to the fact that the emission maxima of the oxadiazole-based homopolymer at about 360 nm, (24, 25) overlaps with the absorption maximum of the terfluorene moiety resulting in emission only from the latter unit. Furthermore, when the excitation wavelength is at the absorption maxima of the terfluorene moiety in solution, the emission intensity is higher compared to the emission intensity caused when the excitation wavelength is at the absorption maxima of the oxadiazole based part (Figure 6a). On the contrary, the emission intensity of the terfluorene segment is much higher in the solid state when the excitation wavelength is at the absorption maximum of the oxadiazole based part, (Figure 6b) showing that the energy transfer from the oxadiazole units is more efficient in the solid state.

Table 2. Optical data of the scTFPOXD and scTFPCARBZ in chloroform solutions and in solid state

Polymers	λ_{abs} (nm) solution	λ_{abs} (nm) film	λ_{PL} (nm) solution^a	λ_{PL} (nm) film^a
scTFPOXD	296, 362	298, 370	411, 429, 465	430, 466
scTFPCARBZ	350	350	417, 431, 468	417, 431, 468

^{a}excitation at the higher wavelength of the absorption spectra.

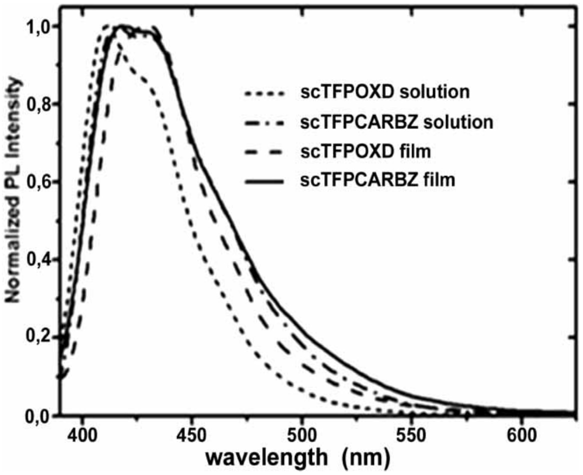


Fig. 5. Photoluminescence spectra of scTFPOXD and scTFPCARBZ in chloroform solutions and as thin films.

As we examined the optical properties of the random copolymers scTFPOXD and scTFPCARBZ in solution and as pristine films, further studies upon photo-oxidation treatment in air were also performed. 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. Both copolymers, except from the efficient quenching of the intra-chain emission (Figures 7a–b) due to the creation of keto defects which act as efficient exciton traps, the appearance of the emission band at 520 nm is also observed (inset of Figures 7a–b) upon UV treatment for different periods of time. In a previous work (14), the same terfluorene segment combined with polystyrene flexible units didn't show the undesired low energy emission band at 520 nm, despite the fluorenone formation, after the same photo-oxidation treatment. The high molecular weight polystyrene flexible block was capable for preventing the inter-segment interactions between the fluorenone units, hence no form of the 520 nm emission band was observed. As a consequence, in this work we can safely conclude that the appearance of the 520 nm emission band is attributed to the fact that the poly(oxadiazole) and polycarbazole matrices in scTFPOXD and scTFPCARBZ

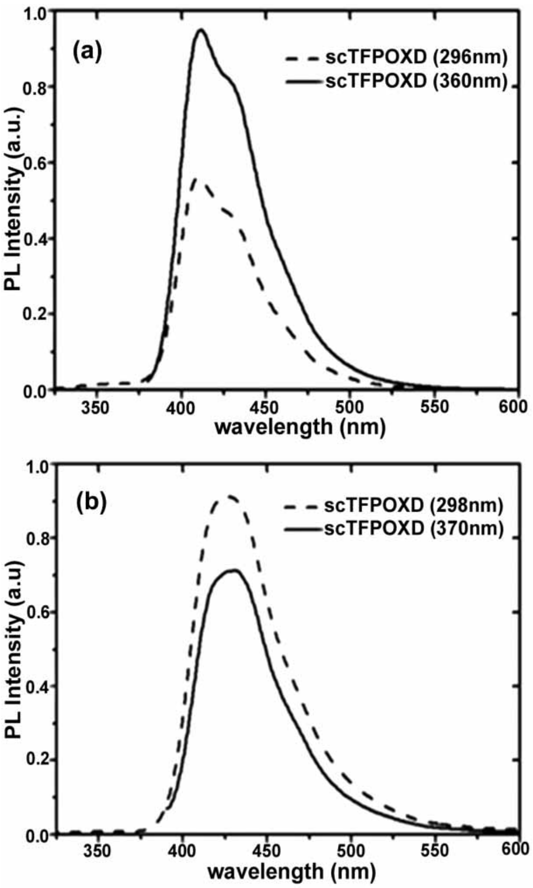


Fig. 6. Photoluminescence spectra of scTFPOXD (a) in chloroform solution and (b) as thin film. Excitation wavelengths at the absorption maxima both in solution and in solid state.

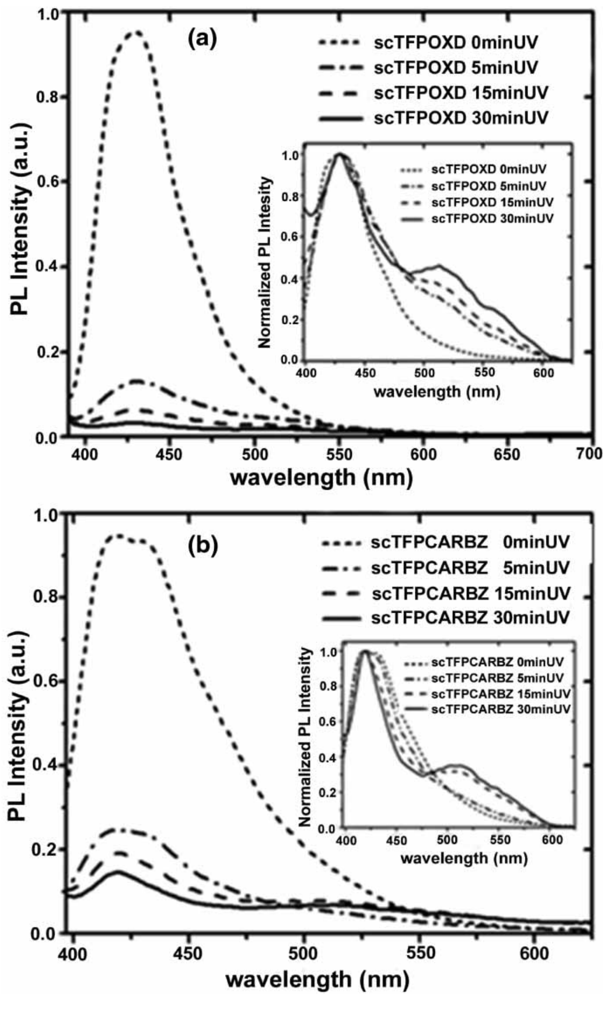


Fig. 7. Photoluminescence spectra of (a) scTFPOXD and (b) scTFPCARBZ in the solid state before and after UV treatment in air (exposure for different periods of time, 5 to 30 min) in arbitrary units. In the insets, the normalized PL spectra of the scTFPOXD and scTFPCARBZ are presented.

copolymers cannot prevent the inter-segment interactions between the terfluorene units upon fluorenone formation. Thus, the random copolymerization approach seems not able to eliminate the 520 nm emission band after UV treatment.

4 Conclusions

Novel random copolymers consisting of terfluorene segments with hole or electron transporting moieties have been effectively synthesized and characterized with a variety of spectroscopic techniques, such as ^{1}H-NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), cyclic voltammetry, FT-IR spectroscopy, UV-Vis and photoluminescence spectroscopy. FT-IR spectroscopy revealed the generation of the carbonyl stretching mode of the fluorenone moiety upon photo-oxidation treatment for different periods of time. Moreover, an efficient energy transfer was detected from the oxadiazole-based homopolymer to the terfluorene block both in solution and in the solid state. Finally, the appearance of the 520 nm emission band for the random copolymers upon UV-treatment in air was exposed, showing that the random polymerization approach of an oligofluorene segment with different vinyl monomers is not capable of preventing the inter-segment interactions.

5 Acknowledgment

Financial support for this project from the Greek Ministry of Development under the research grant EPAN E13 is gratefully acknowledged.

6 References

1. Leclerc, M. (2001) *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 2867.
2. Neher, D. (2001) *Macromol. Rapid. Commun.*, **22**, 1365.
3. Scherf, U. and List, E.J.W. (2002) *Adv. Mater.*, **14**, 477.
4. Sainova, D., Neher, D., Dobruchowska, E., Luszczynska, B., Glowacki, I., Ulanski, I., Nothofer, H.-G. and Scherf, U. (2003) *Chem. Phys. Lett.*, **371**, 15.
5. Bliznyuk, V.N., Carter, S.A., Scott, J.C., Klaerner, G., Miller, R.D. and Miller, D.C. (1999) *Macromolecules*, **32**, 361.
6. Chochos, C.L., Tsolakis, P.K., Gregoriou, V.G. and Kallitsis, J.K. (2004) *Macromolecules*, **37**, 2502.
7. Surin, M., Hennebicq, E., Ego, C., Marsitzky, D., Grimsdale, A.C., Müllen, K., Brédas, J.-L., Lazzaroni, R. and Leclere, P. (2004) *Chem. Mater.*, **16**, 994.
8. Chen, X., Tseng, H.-E., Liao, J.-L. and Chen, S.-A. (2005) *J. Phys. Chem. B*, **109**, 17496.
9. Kulkarni, A.P., Kong, X. and Jenekhe, S.A. (2004) *J. Phys. Chem. B*, **108**, 8689.
10. FRomaner, L., Pogantsch, A., Scandiucci de Freitas, P., Scherf, U., Gaal, M., Zojer, E. and List, E.J.W. (2003) *Adv. Funct. Mater.*, **13**, 597.
11. Chi, C., Im, C., Enkelmann, V., Ziegler, A., Lieser, G. and Wegner, G. (2005) *Chem. Eur. J.*, **11**, 6833.
12. Li, J., Li, M. and Bo, Z. (2005) *Chem. Eur. J.*, **11**, 6930.
13. Sims, M., Bradley, D.D.C., Ariu, M., Koeberg, M., Asimakis, A., Grell, M. and Lidzey, D.G. (2004) *Adv. Funct. Mater.*, **14**, 765.
14. Chochos, C.L., Kallitsis, J.K. and Gregoriou, V.G. (2005) *J. Phys. Chem. B*, **109**, 8755.
15. Zhao, W., Cao, T. and White, J.M. (2004) *Adv. Funct. Mater.*, **14**, 783.
16. Montilla, F. and Mallavia, R. (2007) *Adv. Funct. Mater.*, **17**, 71.
17. Kulkarni, A.P., Tonzola, C.J., Babel, A. and Jenekhe, S.A. (2004) *Chem. Mater.*, **16**, 4556.
18. Morin, J.-F., Leclerc, M., Ades, D. and Siove, A. (2005) *Macromol. Rapid Commun.*, **26**, 761.
19. Yang, N.C., Park, Y.H. and Suh, D.H. (2003) *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 674.
20. Zhan, X., Liu, Y., Wu, X., Wang, S. and Zhu, D. (2002) *Macromolecules*, **35**, 2529.
21. Ding, J., Day, M., Robertson, G. and Roovers, J. (2002) *Macromolecules*, **35**, 3474.
22. Boiteau, L., Moroni, M., Hilberer, A., Werts, M., de Boer, B. and Hadziioannou, G. (2002) *Macromolecules*, **35**, 1543.
23. Li, Y., Ding, J., Day, M., Tao, Y., Lu, J. and D'iorio, M. (2004) *Chem. Mater.*, **16**, 2165.
24. Tzanetos, N.P. and Kallitsis, J.K. (2004) *Chem. Mater.*, **16**, 2648.
25. Tzanetos, N.P. and Kallitsis, J.K. (2005) *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 1049.
26. Miyaura, N. and Suzuki, A. (1995) *Chem. Rev.*, **95**, 2457.
27. Brédas, J.L., Silbey, R., Boudreux, D.S. and Chance, R.R. (1983) *J. Am. Chem. Soc.*, **105**, 6555.
28. Cui, Y., Zhang, X. and Jenekhe, S.A. (1999) *Macromolecules*, **32**, 3824.
29. Leeuw, D.M., Simenon, M.M.J., Brown, A.R. and Einerhand, R.E.F. (1997) *Synth. Met.*, **87**, 53.
30. Silverstein, R.M., Bassler, G.C. and Morrill, T.C. *Spectroscopic Identification of Organic Compounds*; Wiley-VCH: New York, 1981.
31. Gamerith, S., Gadermaier, C., Scherf, U. and List, E.J.W. (2004) *Phys. Stat. Sol. (A)*, **201**, 1132.
32. Chochos, C.L., Papakonstandopoulou, D., Economopoulos, S.P., Gregoriou, V.G. and Kallitsis, J.K. (2006) *J. Macrom. Sci., Pure Appl. Chem. A*, **43**, 419.
33. Liu, L., Tang, S., Liu, M., Xie, Z., Zhang, W., Lu, P., Hanif, M. and Ma, Y. (2006) *J. Phys. Chem. B*, **110**, 13734.
34. Tsolakis, P.K. and Kallitsis, J.K. (2003) *Chem. Eur. J.*, **9**, 936.
35. Chochos, C.L., Kallitsis, J.K., Keivanidis, P.E., Baluschev, S. and Gregoriou, V.G. (2006) *J. Phys. Chem. B*, **110**, 4657.
36. Jiang, X., Killeen, K.A., Thompson, M.E., Pschenitzka, F., Sturm, J.C. and Register, R.A. (2000) *Chem. Mater.*, **12**, 2542.
37. Chen, Z., Liu, Y., Zhang, C. and Bai, F. (2004) *J. Appl. Polym. Sci.*, **92**, 2777.