Aromatic Copolyimides Containing Perylene Units

Radu-Dan Rusu, Mariana-Dana Damaceanu, Maria Bruma*

Summary: Perylene-containing copolyimides have been synthesized by one-step polycondensation reaction under high temperature of two different aromatic diamines with a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA). The copolyimides were soluble in polar amidic solvents and their solutions gave flexible thin films when spread onto glass plates. Very thin films obtained by spin coating had smooth surfaces and were self-organized into vertically segregated structures. The polymers were highly thermostable, their decompositions being above 470 °C and displayed reasonable high glass transition temperature values. After being excited with UV light, the polymers emitted light in the bluish and green-yellow domains.

Keywords: high thermostability; photoluminescence; polyimides; thin films

Introduction

Perylene imides represent a class of highly thermostable *n*-type semiconductors exhibiting relatively high electron affinity among large-band-gap materials.[1] They are also well known chromophores combining high quantum yield of photoluminescence with outstanding photochemical and thermal stability.[2] Inspired by their unique properties, some low molecular weight perylenediimides and polymers containing perylenediimide units in the main chain have been successfully used in light-emitting diodes,[3,4] photovoltaic devices,[5,6] etc. However, the actual application of perylene-containing polyimides was hampered by their poor solubility and low solid-state fluorescence quantum efficiency.[7,8]

The use of 1,3,4-oxadiazole ring in the construction of copolyimides is based on the already known high performance properties of aromatic polyoxadiazoles, such as high thermal resistance, good hydrolytic stability, low dielectric constant, tough mechanical behaviour, and other special properties determined by the electronic structure of this particular heterocycle that has a strong electron-withdrawing character.[9,10] Poly(arylene-oxadiazole)s give easily redox reactions, chemically or electrochemically, and the resulting materials are good candidates for electrochemical sensors or electroluminescent devices, to be used in optoelectronics, microelectronics or other advanced fields.[11–14] There is currently much interest in high-brightness blue light-emitting diodes for use in full colour displays, full colour indicators and light sources for lamps, with characteristics of high efficiency and high reliability. For such a purpose polyoxadiazoles are very attractive because, due to the electron-withdrawing character of the 1,3,4-oxadiazole rings, they can facilitate the injection and transport of electrons.

On the other hand, it was shown that the inclusion of hexafluoroisopropylidene into polymers can increase the solubility, thermal stability, oxidation resistance, transparency and environmental stability. The bulky hexafluoroisopropylidene groups also serve to increase the free volume of the polymers, thus improving their electrical insulating characteristics.[15,16]

The incorporation of oxadiazole together with perylene rings and flexible hexafluoroisopropylidene groups into the polymer

---

"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Gr. Ghica Voda 41A, Iasi-700487, Romania
E-mail: radu.rusu@icmpp.ro

chain is expected to provide a good combination of high performance properties and good processability, particularly in thin films and coatings, with photoluminescent properties for future use as advanced materials in electroluminescent devices.

Synthesis

4,4'-Oxydianiline, **Ia** , *perylene-3,4,9,10-tetracarboxylic dianhydride* (PTCDA), **IIa**, and *4,4'-hexafluoroisopropylidene diphthalic anhydride* (6FDA), **IIb**, whose structures are shown in Figure 1, have been purchased from Aldrich and used as received. *2,5-Bis (p-aminophenyl)-1,3,4-oxadiazole*, **Ib**, has been prepared by a known procedure[17] and its structure is shown in Figure 1.

Copolyimides **III** and **IV** have been prepared by one-step polycondensation reaction of two different aromatic diamines, **I**, with a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride and 4,4'-hexafluoroisopropylidene-diphthalic anhydride, **II**, in N-methylpyrrolidinone (NMP) and lithium chloride (LiCl), as solvent, at a concentration of 7% total solids, under nitrogen stream, at high temperatures.

In case of the two dianhydrides with different reactivity, the less active dianhydride monomer PTCDA was added in the first stage of reaction to the solution of diamine in NMP + LiCl, and then the more active dianhydride monomer 6FDA was added to achieve an even more random incorporation of the two monomer units in the polymer chain. Owing to the low solubility of PTCDA in NMP + LiCl at room temperature, higher reaction temperature is necessary to make better solubility. The mixture was heated to 180–200 °C under nitrogen for 6 h and then cooled to room temperature. Part of the resulting dark red solution was poured into water, washed with plenty of water and finally treated with ethanol in a Soxhlet apparatus for 1 day in order to get rid of the unreacted monomers and high boiling solvent, followed by drying in an oven, under vacuum, at 100 °C. The other part of the polymer solution was used to prepare thin films. The structures of copolyimides **III** and **IV** are shown in Figure 2.

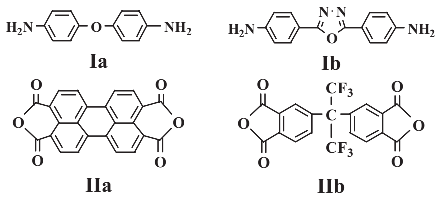


Figure 1.
Structures of the monomers.

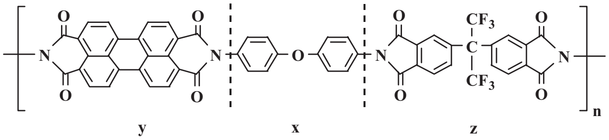
Films of polymers **III** and **IV** were prepared by casting a polymer solution of 7% concentration in NMP + LiCl onto glass plates, followed by gradual heating from room temperature up to 200 °C, and kept at 200 °C for 1 h. Dark-red, opaque coatings resulted having strong adhesion to the glass support. The resulting films were stripped off the plates by immersion in hot water, followed by drying in oven at 105 °C. These films had the thickness in the range of 30–80 μm and were used afterwards for various measurements.

Very diluted polymer solutions in NMP with concentration of 0.5–1% were used to obtain very thin films having the thickness in the range of nanometers onto silicon wafers by spin-coating technique, at a speed of 5000 rpm. These films, as-deposited, were gradually heated up to 180 °C in the same way as described earlier to remove the solvent and were used for atom force microscopy (AFM) investigations.

Measurements

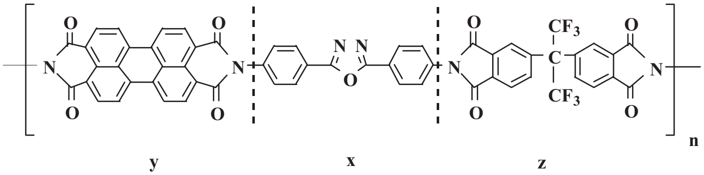
The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets or thin films having the thickness of 5–6 μm.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM +) by means of the HyperChem program, Version 7.5. The same program was used to visualize the structures obtained



x : y : z = 2 : 1 : 1

III



IVa: x : y : z = 2 : 1 : 1
IVb: x : y : z = 3 : 1 : 2
IVc: x : y : z = 4 : 1 : 3

IV

Figure 2.
Structures of copolyimides **III** and **IV**.

after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles). The quality of very thin films as-deposited on silicon plates was investigated by atom force microscopy (AFM) using a Scanning Probe Microscopy Solver PRO-M, NT-MDT equipment made in Russia, in the semi-contact mode, semi-contact topography technique.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a MOM derivatograph, made in Budapest, Hungary, operating at a heating rate of 12 °C/min, in air, from room temperature to 600 °C. The temperature of 5% weight loss was considered the beginning of decomposition or the initial decomposition temperature (IDT). The temperature of maximum rate of decomposition which is the maximum signal in differential thermogravimetry (DTG) curves was also recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined by using a Pyris Diamond DSC, Perkin Elmer calorimeter. Approximately 3 to 8 mg of each polymer were crimped in aluminum pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380 °C at 10 °C/min. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature values of the polymers.

The UV-Vis absorption and photoluminescence spectra of polyimides were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions.

Results and Discussion

One-step polycondensation reaction of equimolar amounts of aromatic diamines **I** with a mixture of PTCDA and 6FDA, in NMP + LiCl as solvent, yielded copolyimides **III** and **IV**. The oxadiazole-containing copolyimides **IV** are based on hexafluoroisopropylidene diphthalic anhydride and perylene-3,4,9,10-tetracarboxylic dianhydride, while the related copolyimide **III** is based on 4,4'-oxydianiline and the same dianhydrides.

The structures of the present polymers were identified by infrared spectra. In the IR spectra of all the polyimides characteristic imide ring absorption bands appeared at 1770–1780 cm^{-1} (asymmetrical C=O imide stretching), 1720–1730 cm^{-1} (symmetrical C=O imide stretching) and 720–730 cm^{-1} (imide ring deformation). It was observed that the broad IR absorption band at 3350–3450 cm^{-1} characteristic of NH amidic linkage and the narrow absorption peak at 1650–1660 cm^{-1} due to C=O linkage in amide group, which are generally present in the spectra of polyamidic acids, disappeared almost completely, which means that the conversion of the intermediate polyamidic acid into final polyimide structure was quantitative by polycondensation in solution at high temperatures. Characteristic absorption peaks of 1,3,4-oxadiazole ring appeared at 960–970 cm^{-1} and 1012 -1020 cm^{-1} (=C−O−C= stretching). C-H linkage in aromatic rings showed absorption peak at 3100 -3120 cm^{-1}, while the C-F linkage showed absorption peak in the range of 1100 -1300 cm^{-1} (Figure 3).

Copolyimides **III** and **IV** are soluble in aprotic amidic solvents such as N-methylpyrrolidinone and pyridine, while related polyimides without 6F and oxadiazole units are insoluble in such solvents, being only soluble in *m*-cresol due to the rigid nature of perylenediimide unit which dictates the overall shape of the corresponding macromolecules and thus facilitates the strong interchain interactions. The better solubility of copolyimides **IV** is explained by the presence of 6F groups that disturb the packing of the polymer chains to some extent, thus, allowing the diffusion of solvent molecules. Representative molecular models of these copolyimides, as visualized by molecular modeling, are shown in Figure 4.

All these copolyimides are highly thermostable, as evaluated by thermogravimetric analysis, their initial decomposition temperature being above 470 °C (Table 1). The temperature of 10% weight loss ranges from 480 to 508 °C. The temperature of maximum rate of decomposition was found in the domain of 528 °C–540 °C. These data demonstrate that all the polyimides have high thermal stability, which is not affected by the introduction of flexible 6F unit in the main chain, while the solubility, hence the processability, of the resulting copolymers is much improved due to the presence of this group. The increase of 6F content from polymer **IVa** to **IVc** has only a very slight influence on the increase of thermal stability. Also, the presence of oxadiazole rings does not have significant influence on the thermal stability of polymers **IV**.

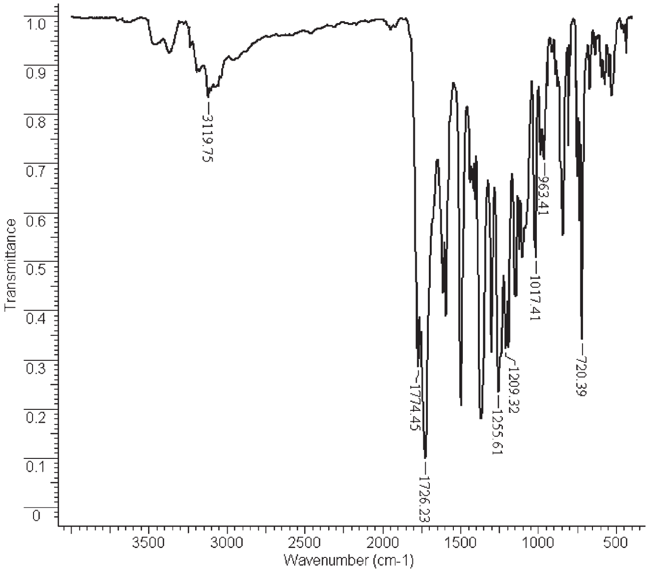


Figure 3.
FTIR spectrum of the polymer **IVc**.

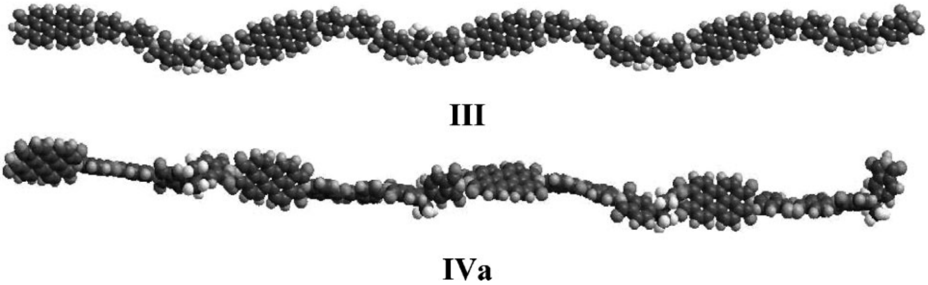


Figure 4.
Models of polyimides based on perylene and hexafluoroisopropylidene units.

The glass transition temperature of the polyimides was evaluated by differential scanning calorimetry (DSC). All these polymers exhibit glass transition in the range of 245–292 °C (Table 1, Figure 5). Polymer **IVc** shows a second endothermic peak in the DSC traces. Such weak transition is characteristic of liquid crystalline perylene-containing polyimides due to the strong interactions between the perylene moieties.[18] These data correlated with AFM results may indicate some degree of ordering and will be investigated in the future. It can be seen that there is a large interval between T_g and decomposition temperature of these copolyimides, which can be advantageous for their processing by a thermoforming technique, as well. Typical thermogravimetric curves are shown in Figure 6.

Copolymers **III** and **IVa** gave free standing films by casting 7% polymer solutions onto glass plates. Such films had the thickness in the range of tens of micrometers and were flexible and creasable, and resisted to repeated bendings. The films obtained from polymers **IVb** and **IVc** were brittle.

Table 1.
Thermal properties of the polymers.

Polymer	T_g (°C)	IDT (°C)	$T_{10\%}$ (°C)	T_{max} (°C)
III	245	475	508	540
IVa	265	470	480	528
IVb	282	480	485	535
IVc	292	480	496	535

T_g = glass transition temperature.
IDT = temperature of 5% weight loss.
$T_{10\%}$ = temperature of 10% weight loss.
T_{max} = temperature of maximum rate of decomposition.

Very thin films having the thickness in the nanometer range were deposited by spin-coating technique onto silicon plates, by using diluted solutions of polymers **III** and **IV** (concentration of 1%). The morphology of these films as-deposited onto silicon plates was studied by atomic force microscopy (AFM). These spin-coated copolymer films are self-organized into vertically segregated structures. A typical AFM image is shown in Figure 7.

Since 1,3,4-oxadiazole and perylene moieties are known as light emissive units,[19,20] we have performed a study of the UV absorption and photoluminescence (PL) properties of these polyimides. It was found that polymers **IV** show one strong UV absorption peak at 302–320 nm, and three shoulders at 462–464 nm, 492–494 nm and 526–529 nm, in NMP solutions, the spectra being almost identical. The absorption maxima at 302–320 nm of these polymers are mainly determined by the diphenyl-1,3,4-oxadiazole unit, because the unsubstituted diphenyl-1,3,4-oxadiazole in hexane shows its absorption maximum at 284 nm.[21] The absorption peaks at 462–464 nm, 492–494 nm and 526–529 nm are due to the chain segments containing perylenediimide units.[22] Figure 8 presents the UV-vis absorption spectra of polymers **IV** in NMP solutions.

After being excited with UV light of 360 nm, polymers **IV** displayed similar spectra with one strong and large emission

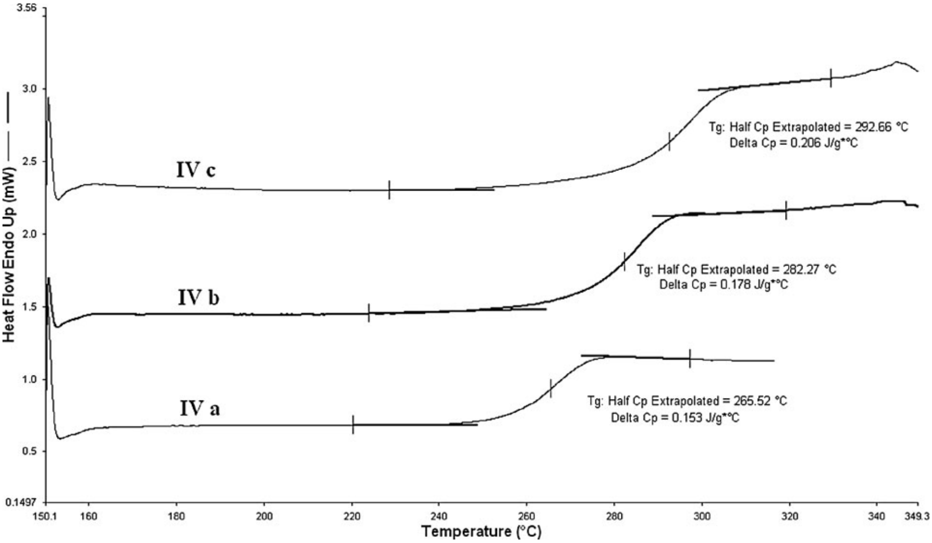


Figure 5.
DSC curves of polymers **IV**.

band centred around 405 nm, in the blue domain, due to the emission of oxadiazole, imide and phenylene rings, and two maxima in the green and yellow spectral range, around 535 nm and 577 nm, respectively, due to the emission of perylenediimide moieties. The excitation with 360 nm of polymer **III,** which does not contain oxadiazole rings, in solution, resulted in a spectrum with two emission maxima in the blue domain at 408 and 442 nm and other two in the green and yellow spectral range,

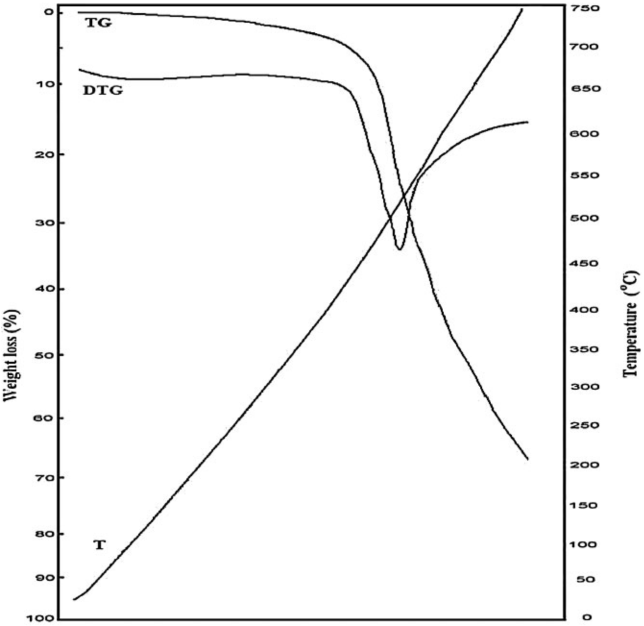


Figure 6.
Thermogravimetric curves of polymer **IVc**.

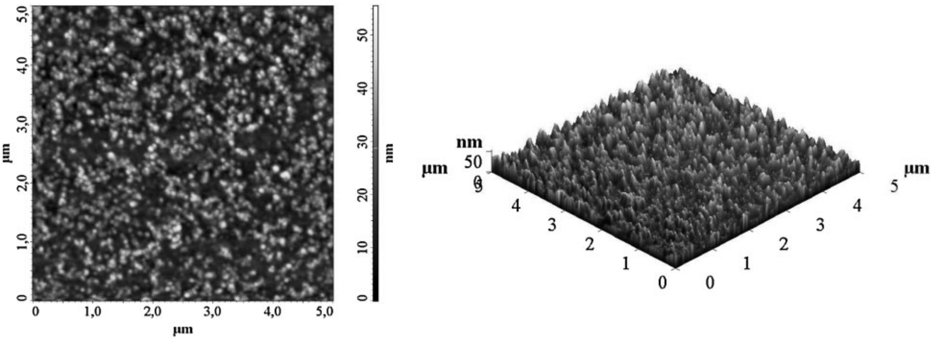


Figure 7.
AFM images of copolyimide **IVa** (left: top-view, right: side-view).

at 538 and 577 nm, due to the emission of perylene units. If in the PL spectra of polymer **III** the most intense peak is due to the perylene chromophore, in the case of polymers **IV** containing oxadiazole rings, the main PL emission bands are determined by the oxadiazole chromophore. The intensity of these bands is comparably higher than those of perylene units which could be explained by an excitation energy transfer from perylenediimide to oxadiazole moieties. The increasing of the 6F contents in polymers **IV** does not affect significantly the position of the emission maxima, while having an important effect upon the solubility and processability of poly(peryleneimide)s. Optical and photoluminescence properties of copolyimides in solution are presented in Table 2.

No emission was observed in the solid state. This is probably due to the high content of perylene cromophore which leads to fluorescence quenching through aggregation. Figure 9 shows the photoluminescence spectra of copolyimides **III** and **IV**.

Table 2.
Optical and photoluminescence properties of copolyimides in solution.

Polymer	UV, sol	PL (at 360 nm)
	λ_{max}, nm	λ_{em}, nm
III	375, 459, 492, 528	408, 442, 538, 577
IVa	313, 464^s, 492, 529	404, 534, 586^s
IVb	303, 492, 526	406, 534, 577^s
IVc	303, 494, 528	406, 533, 586

λ_{max} - wavelength of the maximum absorption peak.
λ_{em} - wavelength of the maximum PL peak.
^{s}- shoulder.

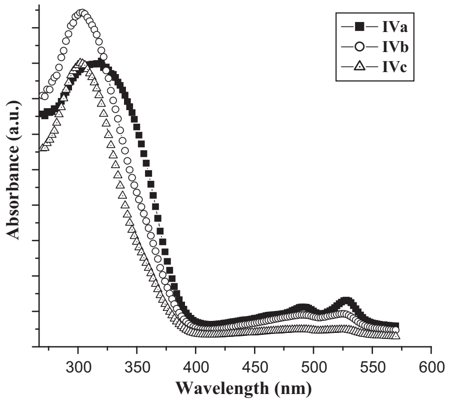


Figure 8.
UV-vis absorption spectra of polymers **IV**.

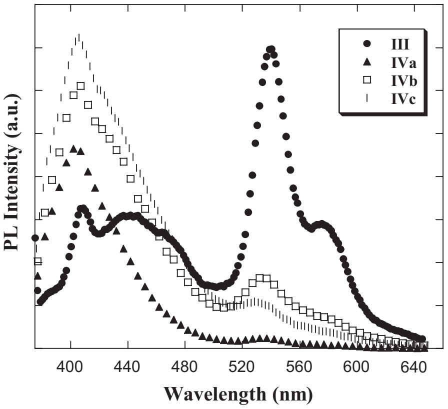


Figure 9.
Photoluminescence spectra of copolyimides **III** and **IV**.

Conclusion

The introduction of flexible 6F groups into the chain of perylene-containing polyimides gave polymers with good solubility in polar amidic solvents, while related poly(peryleneimide)s without 6F groups are completely insoluble. These polyimides based on perylene and hexafluoroisopropylidene units can be processed into thin flexible films having the thickness in the range of tens of micrometers using casting technique. Very thin films with thickness in the range of nanometres obtained by spin-coating technique exhibited smooth surface, without peaks and pinholes. All the polyimides showed high thermal stability, with decomposition temperature being above 470 °C, and glass transition in the range of 245–295 °C, with a large interval between decomposition and glass transition temperatures. All the polyimides exhibited photoluminescence in solution after being excited with UV light of 360 nm, with strong maxima of photoluminescence in the range of 405–410 nm, 530–535 nm and 575–580 nm. Such properties make the present polyimides attractive for applications in advanced opto-electronics and other related fields.

Acknowledgements: The financial support provided by the Romanian Program PNCD-2, contract no. 11008/2007 is acknowledged with great pleasure. The authors thank to C. Grigoras from ICMPP - Iasi for DSC measurements.

[1] X. W. Zhan, Z. A. Tan, B. Demercq, Z. S. An, X. Zhang, S. Barlow, Y. F. Li, D. B. Zhu, B. Kippelen, S. R. Marder, *J. Am. Chem. Soc.*, **2007**, *129*, 7246.

[2] H. Y. Wang, K. Y. Pu, S. Huang, F. Liu, B. Peng, W. Wei, *React. & Funct. Polym.*, **2009**, *69*, 117.

[3] P. Schouwink, A. H. Schäfer, C. Seidel, H. Fuchs, *Thin Solid Films*, **2000**, *372*, 163.

[4] M. Schneider, J. Hagen, D. Haarer, K. Müllen, *Adv. Mater.*, **2000**, *12*, 351.

[5] Y. J. Kim, A. J. Bard, *Chem. Phys. Lett.*, **2004**, *383*, 11.

[6] H. J. Niu, C. Wang, X. D. Bai, Y. D. Huang, *Polym. Adv. Technol.*, **2004**, *15*, 701.

[7] S. Xu, M. Yang, S. Cao, *React. & Funct. Polym.*, **2006**, *66*, 471.

[8] S. Xu, Y. Jin, M. Yang, F. Bai, S. Cao, *Polym. Adv. Technol.*, **2006**, *17*, 556.

[9] B. Schulz, M. Bruma, L. Brehmer, *Adv. Mater.* **1997**, *9*, 601.

[10] M. D. Damaceanu, R. D. Rusu, M. Bruma, A. L. Rusanov, *Polym. Adv. Technol.*, DOI: 10.1002/pat.1519.

[11] P. E. Cassidy, T. M. Aminabhavi, V. S. Reddy, in: "*Kirk Othmer Encyclopedia of Chemical Technology 4ed*", vol. 12, J. I. Kroschwitz, Ed., John Wiley & Sons, New York 1994, p. 1045–1070.

[12] B. Schulz, L. Brehmer, in: "*Polymeric Materials Encyclopedia*", vol. 7, J. Salamone, Ed., CRC Press, Boca Raton 1996, p. 5595–5604.

[13] X. C. Li, G. C. W. Spencer, A. B. Holmes, S. C. Moratti, F. Cacialli, R. H. Friend, *Synth. Met.*, **1996**, *76*, 153.

[14] S. Janietz, B. Schulz, *Eur. Polym. J.*, **1996**, *32*, 465.

[15] M. Bruma, J. W. Fitch, P. E. Cassidy, *J. Macromol. Sci. Phys. C*, **1996**, *36*, 119.

[16] P. E. Cassidy, J. W. Fitch, in: "*Modern Fluoropolymers*", J. Schiers, Ed., John Wiley & Sons, New York 1997, p. 173–190.

[17] A. L. Rusanov, L. B. Elshina, E. G. Bulyceva, K. Müllen, in: "*Polymer Yearbook*", vol. 18, R., Pethrick, G. Zaikov, Eds., Rapra Technology, Shropshire 2004, p. 7–47.

[18] D. Yao, Y. Z. Wang, P. R. Sundararajan, *Polymer* **2005**, *46*, 4390.

[19] J. Hil, in: "*Comprehensive Heterocyclic Chemistry*", vol. 6, A. R. Katrittzky, Ed., Pergamon Press, Oxford 1984, p. 427–446.

[20] L. Akcelrud, *Prog. Polym. Sci.*, **2003**, *28*, 875.

[21] M. D. Iosip, M. Bruma, J. Robison, Y. Kaminorz, B. Schulz, *High Perform. Polym.*, **2001**, *13*, 133.

[22] F. Nolde, W. Pisula, S. Muller, C. Kohl, K. Mullen, *Chem. Mater.*, **2006**, *18*, 3715.