Macromol. Symp. **2004**, *212,* 83-91

Materials for Polymer Electronics Applications – Semiconducting Polymer Thin Films and Nanoparticles

U. Asawapirom,[1] *F. Bulut,*[2] *T. Farrell,*[1] *C. Gadermaier,*[5] *S. Gamerith,*[5] *R. Güntner,*[1] *T. Kietzke,*[3] *S. Patil,*[1] *T. Piok,*[5] *R. Montenegro,*[4] *B. Stiller,*[3] *B. Tiersch,*[1] *K. Landfester,*[4] *E. J. W. List,*[5] *D. Neher,*[3] *C. Sotomayor Torres,*[2] *U. Scherf**[1]

[1] Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str.24/25, Haus 25, 14476 Golm, Germany
E-mail: scherf@rz.uni-potsdam.de
[2] BUGH Wuppertal, FB Elektrotechnik, Gaußstr.20, 42097 Wuppertal, Germany
[3] Universität Potsdam, Institut für Physik, Am Neuen Palais 10, D-14469 Potsdam, Germany
[4] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, 14424 Golm, Germany
[5] TU Graz, Institut für Festkörperphysik, Petersgasse 16, 8010 Graz, Austria

Summary: The paper presents two different approaches to nanostructured semiconducting polymer materials: (i) the generation of aqueous semiconducting polymer dispersions (semiconducting polymer nanospheres SPNs) and their processing into dense films and layers, and (ii) the synthesis of novel semiconducting polyfluorene-*block*-polyaniline (PF-*b*-PANI) block copolymers composed of conjugated blocks of different redox potentials which form nanosized morphologies in the solid state.

Keywords: block copolymer; nanoparticle; nanostructure; polyaniline; polyfluorene; semiconducting polymer

Introduction

Solid layers of conjugated polymers have been successfully included as active layers into various electrical and electrooptical devices such as light-emitting diodes (LEDs),[1] solar cells[2] and field-effect transistors (FETs).[3] In most cases, these layers have been deposited from solutions of the polymers in organic solvents. However, deposition from those solvents brings about several problems, in particular when dealing with large-area or multilayer devices; the deposition from aqueous systems would be most desirable. Recently, polymer conductors, such as poly[(ethylenedioxy)thiophene] (PEDOT) doped with poly(styrenesulfonate) (PSS) have been deposited from water-based dispersion,[4] but this approach is focused on the deposition of

DOI: 10.1002/masy.200450808

electrically conducting polyelectrolytes (PEDOT, or polyaniline PANI). Very recently, we could demonstrate for the first time the film formation from semiconducting, preferably fluorescent polymer nanospheres (SPN), deposited onto solid substrates from aqueous dispersions.[12]

For LED and FET applications, the active semiconducting polymers are mostly used as single-component materials, such as isotropic films or layers of uniform morphology. For other applications, in particular the use of conjugated materials in photovoltaic devices (solar cells, photodetectors), more complex materials have become more and more attractive. [5,6] The efficiency of such devices is often limited by the short exciton diffusion range in conjugated polymers relative to their optical absorption depth. Structures in which a heterojunction is distributed throughout the film have become increasingly important, e.g. conjugated polymers doped with fullerene acceptors or fullerene/polymer multilayer systems.[7,8] Since only the light absorbed close to the heterojunction between the components results in charge generation, the width of this active region is limited by the exciton diffusion range of photogenerated charge carriers (in conjugated polymers typically 10-20 nm [9,10]). Novel systems, which are able to undergo internal nano- and microphase separation, came in the focus of interest, since such micro- or nanoscopically structured systems allow for an effective charge separation (and transport) of optically generated electron/hole pairs.

Several approaches to the generation of such systems have been used: (i) Mixtures of two immiscible polymers can segregate (demix) to complex, phase-separated structures.[11] The length scale of phase separation is often in the "meso" length regime (10-100 nm), and is convenient but often less controlled. (ii) Semiconducting polymer nanospheres (SPNs) can be processed with a second, bulk component into nanostructured heterojunction composites. (iii) In conjugated-conjugated block copolymers the scale length of phase separation and the electronic nature of the phases is expected to be directly related to the chemical structure and the length of both blocks. It will be possible to fine-tune the scale length of phase separation to be in the range of the diffusion lengths of the (optically formed) excitons. That would allow for a sufficient charge carrier transport of holes and electrons.

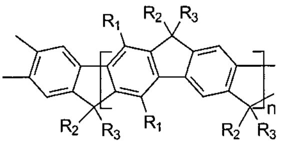
Such conjugated-conjugated block copolymers represent a so far unknown class of electronically active polymers. In particular those composed of two conjugated blocks of different oxidation and reduction potentials are very attractive. If they form suited nanophase- and microphase-separated structures, efficient charge separation can occur, favourably followed by an efficient transport of the charge carriers to the corresponding electrodes.

Semiconducting Polymer Nanospheres

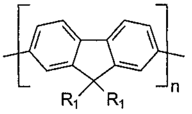
We could recently demonstrate for the first time the film formation from semiconducting, preferably fluorescent polymer nanospheres (SPN), deposited onto solid substrates from aqueous dispersions. [12]

Nanoparticles from semiconducting polymers in aqueous phase have been produced via the miniemulsion process. Miniemulsions are understood as stable emulsions consisting of stable droplets with a size of 50 - 500 nm by shearing a system containing oil, water, a surfactant, and a highly water-insoluble compound, the so-called hydrophobe.[13,14] The surfactant stabilizes the droplets against collisions; mass exchange (Ostwald ripening) between the droplets is suppressed by the use of the hydrophobe. For our SPN dispersions, we have started from artificial latexes consisting of a solution of the preformed semiconducting polymer. After evaporation of the solvent, the polymer dispersion is obtained.

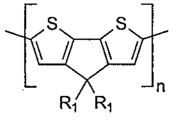
Solutions of different conjugated semiconducting polymers in chloroform (with concentrations between 1.5 and 5.4 %) were successfully miniemulsified in water by using sodium dodecyl sulfate (SDS) as surfactant. Me-LPPP is a solution processable poly(*p*-phenylene)-type ladder polymer which has been widely used as active semiconducting material in electronic devices (light emitting diodes LEDs, solid state lasers, photodiodes).[15,16] Polyfluorene (PF) derivatives are characterized by a unique combination of semiconducting and liquid-crystalline (LC) properties, and have been applied as high-performance blue emitters in LEDs based on organic semiconducting polymers.[17-19] Poly(cyclopentadithiophene)s (PCPDT) as heterocyclic PF analogues are characterized by a reduced band gap (HOMO/LUMO) energy relative to PF, they are promising materials for potential use in organic materials-based field-effect transistors (FETs) and solar cells.[20] After evaporation of the solvent (chloroform), stable polymer dispersions with solid contents of 5-10 % and a polymer particle size of 50-250 nm were obtained.



Me-LPPP



PF



PCPDT

Chemical structure of Me-LPPP (R_1: hexyl, R_2: methyl, R_3: 4-decylphenyl), PF (R_1: 2-ethylhexyl - PF2/6, and 3,7,11-trimethyldodecyl - PF11112, respectively), and PCPDT (R_1: 3,7-dimethyloctyl).

In Figure 1a, a TEM picture of a dispersion with Me-LPPP particles shows spherical and, due to their high T_g, hard particles. It has to be mentioned that for this measurement, the dispersion is highly diluted leading to isolated clusters of particles.

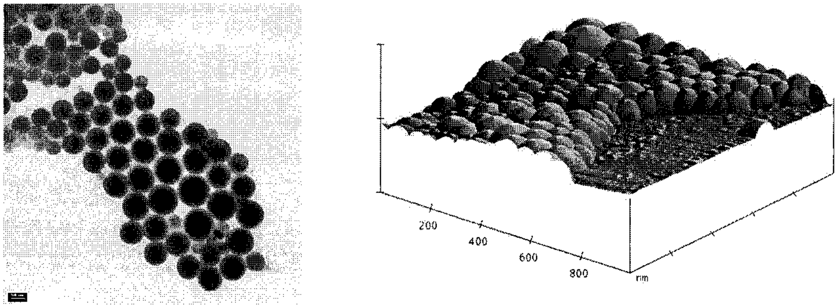


Figure 1: a) (left) TEM picture of Me-LPPP particles; b) (right) 3D AFM picture of semiconducting nanosphere monolayer, prepared by spin-coating a Me-LPPP dispersion on glass (part of the material has been removed by scratching)

Homogeneous layers of SPNs could be prepared by spin-coating the dispersion with the negatively charged particles onto a glass substrate. The resulting films consist of a monolayer of closely packed particles, as seen by AFM; the micrographs do not reveal any cracks within an area of 5 × 5 μm^2 (Figure 1b). Because Me-LPPP has its glass transition temperature well above the onset of decomposition (300-350 °C), the particulate structure also does not change during annealing at 200 °C for 2 h. The absorption and photoluminescence (PL) emission spectra recorded on these films (Figure 2) are identical to those reported for layers of Me-LPPP from organic solvents.[16]

For homogeneous layers of polyfluorene (PF) particles, in contrast to Me-LPPP, annealing of these layers above T_g at 200 °C for 2 h (transition to the birefringent fluid (nematic) LC phase at 100-170 °C [21,22]) results in coalescence of particles and formation of larger structures.

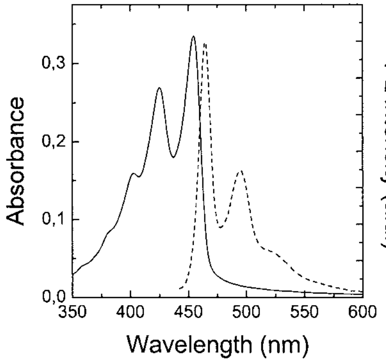
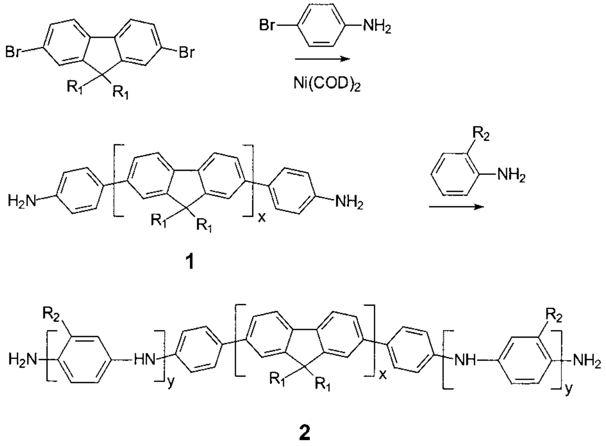


Figure 2: Absorption and photoluminescence spectrum of the SPN layer (Me-LPPP) of Figure 1b

In conclusion, we have shown that layers of conjugated semiconducting polymers can be deposited from aqueous dispersion prepared by the miniemulsion process. Dispersions of particles of different conjugated semiconducting polymers such as a ladder-type poly(*p*-phenylene) and several soluble derivatives of polyfluorene could be prepared with well controllable particle sizes ranging between 50 - 250 nm. Layers of these particles formed by spincoating exhibit a particulate structure, revealing the shape of individual polymer nanoparticles. Annealing above the glass transition temperature of the polymer results in coalescence of particles, larger domains of continuous structure being formed. We, therefore, propose that the concept of semiconducting polymer nanoparticles allows to form multilayer structures by, e.g., depositing a first layer from a solution of a polymer and overcoating it by semiconducting polymer nanospheres of the second polymer from an aqueous phase, followed by annealing and film formation. Most important, this will allow the formation of a multilayer structure from polymers, which are highly soluble in the same solvents, without introducing any additional chemical conversion steps.

Polyfluorene/Polyaniline Block Copolymers

The synthesis of conjugated 9,9-dialkylfluorene/2-alkylaniline block copolymers was described by us in two earlier publications.[23,24] The first step of the today favoured synthetic route towards PF/PANI block copolymers involves the aryl-aryl coupling of 2,7-dibromo-9,9-dialkylfluorenes in the presence of unprotected 4-bromoaniline according to Yamamoto. The coupling reaction leading to prepolymer **1** surprisingly tolerates unprotected 4-aminophenyl functions. In this way, the one-step synthesis of 4-aminophenyl end-functionalized polyfluorenes **1** was carried out. The molecular weight of the polyfluorene prepolymer **1** can be controlled by the feed ratio of bifunctional dibromofluorene/4-bromoaniline. The end-cappers are indeed chemically attached to the prepolymer chains, which can be proved by elemental analysis and ^{1}H NMR spectroscopy. The NMR analysis indicates functionalization with ca. 2.0 4-aminophenyl end groups per prepolymer **1** chain, the PF chains thus being completely terminated with 4-aminophenyl functions.



Synthetic route to polyaniline-*block*-polyfluorene-*block*-polyaniline (PF-*b*-PANI) copolymers.

The second reaction step of our improved PF-*b*-PANI synthesis then involves the oxidative coupling (reagent: $(NH_4)_2S_2O_8/H^+$) of NH_2-terminated prepolymer **1** with 2-undecylaniline. The AB-type character of the aniline monomer guarantees the exclusive formation of PF/PANI block copolymers **2** during this reaction step without crosslinking, branching or multiblock formation. The undecyl-substituted aniline monomer was chosen because of the increased solubility of the corresponding, alkylated PANI building block.[25] The poly(2-undecylaniline) homopolymer is, in contrast to the insoluble unsubstituted polyaniline, slightly soluble in several polar organic solvents (e.g. THF), but insoluble in toluene.[25] Based on this property, the homocoupling product poly(2-undecylaniline), which is formed as (unwanted) side-product remains as insoluble residue during an extraction of the reaction product with toluene.

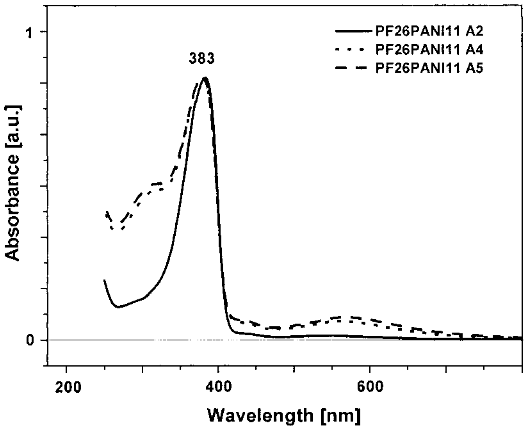


Figure 3: UV-Vis spectra of PF-*b*-PANI block copolymers **2** with different PANI block lengths (R_1: 2-ethylhexyl, R_2: undecyl)

An independent proof that the PANI blocks are really covalently attached to the PF blocks came from GPC analysis with a parallel UV-Vis detection at the distinctly different absorption maxima of the PF (380 nm) and the PANI block (540-560 nm), and RI detection (control experiment). In particular, the identical peak molecular weights M_p indicate, that the absorbing species at ca. 380 and 540-560 nm correspond to molecules with (nearly) identical molecular weights. Also considering the low molecular weight of the poly(2-undecylaniline) homopolymer which is formed as side-product ($M_n < 5000$), these results are a strong proof of the presence of the expected PF/PANI block copolymer **2**.

The UV-VIS spectrum of **2** (Figure 3) indicates the presence of the poly(2-undecylaniline) blocks, for which a red-shifted, low-intensity absorption band centred at ca. 540-560 nm is characteristic (λ_{max} for poly[9,9-bis(2-ethylhexyl))fluorene] homopolymer 385 nm, for poly(2-undecylaniline) homopolymer 550 nm). The relatively weak intensity of the PANI absorption at 540-560 nm is a result of the relatively low absorbance of poly(2-undecylaniline) at this wavelength.

The next step was the characterization of the morphology of **2** by AFM and TEM (Figure 4). First, tapping (contact) mode AFM, and TEM images of block copolymer **2** are depicted in Figure 2: (a) an AFM image of a spin-coated film of a PF/PANI block copolymer **2** (film thickness ca. 100 nm), (b) a TEM image of a spin-coated film of the same block copolymer **2** (film thickness ca. 100 nm).

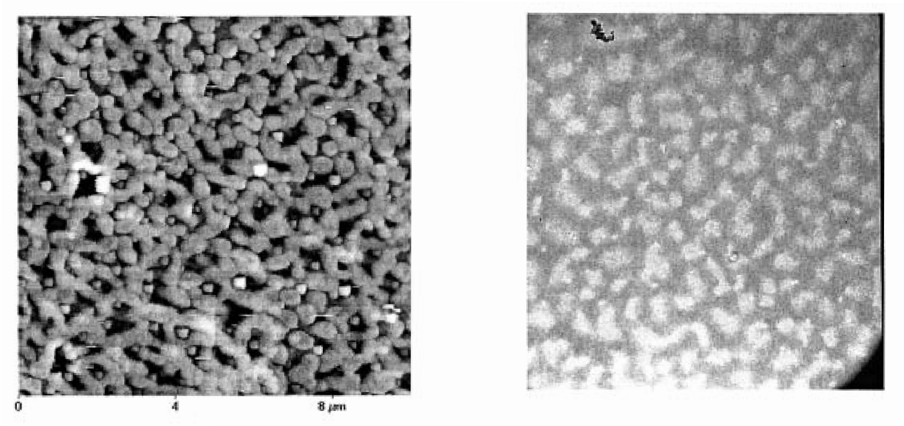


Figure 4: a) (left) AFM image (tapping mode) of a spin-coated film of the PF-*b*-PANI block copolymer **2** (film thickness ca. 100 nm, distance between the arrows: 0.6 µm); b) (right) TEM image of a spin-coated film of the same PF-*b*-PANI block copolymer **2** (film thickness ca. 100 nm)

Clearly, the copolymers self-assemble into branched cylindrical morphologies already during spin-coating, with a diameter of the nanocylinders of ca. 50-300 nm. Annealing (2 h / 200 °C) of the films leads to formation of denser packed films but under conservation of the nanostructered morphology.

In summary, we have developed a simple synthesis of novel PANI-PF-PANI triblock copolymers. The next step will be a more detailed investigation of the formed nanostructures, with respect to the relative and absolute block lengths, as well as the processing conditions.

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.

[2] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, *11*, 15.

[3] A. R. Brown, C. P. Jarrett, D. M. Deleeuw, M. Matters, *Synth. Met.* **1997**, *88*, 37

[4] B. L Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481.

[5] N. S. Sariciftci, A. J. Heeger, *Int. J. Mod. Phys.* **1994**, *B 8*, 237.

[6] N. S. Sariciftci, *Prog. Quantum Electron.* **1995**, *19*, 131.

[7] S. Morita, A. Zakhidov, K. Yoshino, *Solid State Commun.* **1992**, *82*, 249.

[8] B. Kraabel, J.C. Hummelen, D. Vacar, D. Moses, N.S. Sariciftci, A.J. Heeger, F. Wudl, *J. Chem. Phys.* **1996**, *104*, 4267.

[9] A. Haugeneder, C. Kallinger, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, E. Harth, A. Gügel, K. Müllen, in: Z.H. Kafafi (Ed.), *Proc. SPIE* **1997**, *3142*, 140.

[10] A. Haugeneder, M. Neges, C. Kallinger, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, E. Harth, A. Gügel, K. Müllen, *Phys. Rev. B* **1999**, *59*, 15346.

[11] D. Vacar, E. Maniloff, D. McBranch, A.J. Heeger, *Phys. Rev. B* **1997**, *56*, 4573.

[12] K. Landfester, R. Montenegro, U. Scherf, R. Güntner, U. Asawapirom, S. Patil, D. Neher, T. Kietzke, *Adv. Mater.* **2002**, *14*, 651.

[13] K. Landfester, *Macromol. Rapid Commun.* **2001**, *22*, 896.

[14] K. Landfester, *Adv. Mater.* **2001**, *13*, 765.

[15] U. Scherf, *J. Mater. Chem.* **1999**, *9*, 1853.

[16] G. Lanzani, S. De Silvestri, G. Cerullo, S. Stagira, M. Nisoli, W. Graupner, G. Leising, U. Scherf, K. Müllen, "Photophysics of Methyl Substituted Poly(para-Phenylene)-Type Ladder Polymers", in: *Semiconducting Polymers*, G. Hadziioannou and P. F. van Hutten, Eds, Wiley-VCH, Heidelberg, **1999**, Chap. 9, p. 235.

[17] Gross, D. C. Müller, H.-G. Nothofer, U. Scherf, D. Neher, C. Bräuchle, K. Meerholz, *Nature* **2000**, *405*, 661.

[18] T. Miteva, A. Meisel, W. Knoll, H.-G. Nothofer, U. Scherf, K. Müller, K. Meerholz, A. Yasuda, D. Neher, *Adv. Mater.* **2001**, *13*, 565.

[19] D. C. Müller, T. Braig, H.-G. Nothofer, M. Arnoldi, M. Gross, U. Scherf, O. Nuyken, K. Meerholz, *ChemPhysChem* **2000**, *1*, 207.

[20] U. Asawapirom, U. Scherf, *Macromol. Rapid Commun.* **2001**, *22*, 746.

[21] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H.-G. Nothofer, U. Scherf, A. Yasuda, *Adv. Mater.* **1999**, *11*, 671.

[22] U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477.

[23] C. Schmitt, H.-G. Nothofer, A. Falcou, U. Scherf, *Macromol. Rapid Commun.* **2001**, *22*, 624.

[24] R. Güntner, U. Asawapirom, M. Forster, C. Schmitt, B. Stiller, B. Tiersch, A. Falcou, H.-G. Nothofer, U. Scherf, *Thin Solid Films* **2002**, in press.

[25] A. Falcou, D. Marsacq, P. Hourquebie, A. Duchêne, *Tetrahedron* **2000**, *56*, 225.