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Conformational Transitions and Aggregations of Regioregular Polyalkylthiophenes

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Summary: Diverse conformational transitions and aggregations of regioregular poly (3-alkylthiophene)s (PATs) in different environment have been studied by means of AFM and UV-vis-spectroscopy. In methanol, which is a non-solvent for both alkyl side groups and aromatic backbone at low polymer concentration, PATs chains fold into compact poorly ordered flat structures. At higher polymer concentration PATs molecules undergo 3D aggregation into near spherical particles. In hexane, which is a selective solvent for alkyl side chains, PATs molecules undergo ordered main-chain collapse followed by 1D aggregation. Concentration-independent red shift of λmax and good resolved fine vibronic structure in the electronic absorption spectra indicate that planarization occurs on the single-molecule level.

Keywords: atomic force microscopy (AFM); conducting polymers; helical conformation; one-dimensional aggregation; solvatochromism

Introduction

Poly(3-alkylthiophehe)s belong to one of the most studied families of conductive polymers[1] having potential applications such as light-emitting diodes,[2] thin film transistors[3] and chemical sensors.[4] It is well-known that optical properties,[2,5] conductivity,[6] and field-effect mobility[3] strongly depend on single-chain conformation and solid-state packing mode. The presence of flexible side groups does not only enhance the solubility of PATs, but also leads to novel optical effects. Indeed, PATs with regioregular head-to-tail (RRHT) structure show reversible color changes response to the temperature[5,7] or to altering of the solvent quality.[8] The observed red shift in electronic absorption spectra is due to a reversible transition between a nonplanar (less conjugated) and more planar (more conjugated) conformation of the main chain. Despite of extensive experimental and theoretical studies, conformations of PATs in different solvents as

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well as exact structures of their aggregates remain unknown and still extensively discussed. It is generally accepted in the literature to connect the dramatic color change of PATs with the transition from twisted conformation of polymer chains in good solvent into the *planar* rigid-rod one with all-*anti* configuration of aromatic rings (Figure 1a) no matter either such a transformation occurs during evaporation of *good solvents* or upon addition of *non-solvents.*[8]

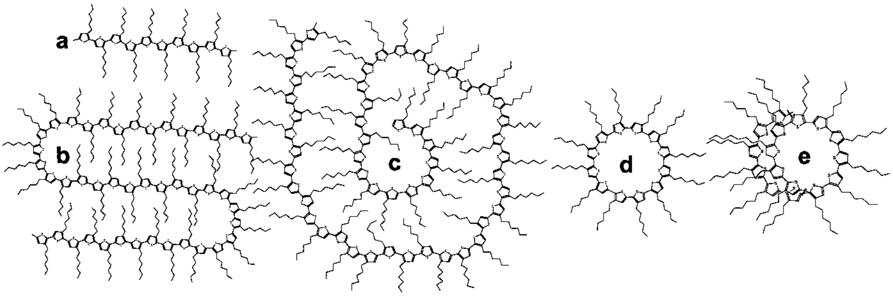

Figure 1. Possible planar conformations of regioregular head-to-tail poly(3-alkyllthiophene): all-anti (rigid-rod) (a); hair-pin (b); spool-like (c); cyclo[12]thiophene (d); all-syn helix (e).

Recently it was shown by scanning tunneling microscopy that polythiophenes backbone capable to adopt some *folded* but still *planar* conformations.[9] For example, an intramolecular hair-pin fold of PATs is composed of seven thiophenes rings in all-*syn* conformation[10] (Figure 1b), whereas larger curvatures include additional *anti*-conformations in the fold (spool-like conformation, Figure 1c). On the other hand, molecular mechanics optimizations[11] of a simple PAT model with 24 thiophene rings show the existence of a helical form with twelve *syn*-connected thiophene units per turn. All sulfur atoms of the helix are directed inside the cavity, whereas hydrocarbon groups oriented outside the helix (Figure 1e). For all structures listed in Figure 1, one can expect considerably red shifted UV-vis spectra (comparably with the spectra taken in good solvents), because they have either completely planar conformation or slightly deviated from planarity.

Here we report on a combined AFM[12] and spectroscopic investigation of the diverse conformation transitions and aggregations of RRHT poly(3-octylthiophene) (POT) and poly(3-hexylthiophene) (PHT) in polar and unpolar solvents. We will show that planar conformations of PATs with high content of syn-configuration of thiophene rings (Figures 1b, c, e) play an important role in the chromic behavior of PATs.

Experimental Section

Materials. POT was purchased from Aldrich. PHT was synthesized via McCullougth method.[13]

Sample preparation. Samples were prepared according procedure reported before.[11]

UV-vis Measurements. UV-vis measurements were carried out using Perkin Elmer UV/vis Spectrometer Lambda 19).

AFM measurements. Multimode AFM instrument (Digital Instruments, Santa Barbara) operating in the tapping mode was used. Silicon tips with radius of 10-20 nm, spring constant of 30 N/m and resonance frequency of 250-300 KHz were used after calibration with the gold nanoparticles (diameter 5 nm) to evaluate the tip radius. The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius.

Results and discussion

In this study we used RRHT polymers: relatively long POT (GPC-data: M_w = 142 kg/mol; PDI = 2.6) and shorter PHT (GPC-data: M_w = 24 kg/mol; PDI = 1.6). On the base of MALDI-TOF data contour length of polymers used in this study equal approximately to L_w = 124nm and L_N = 48nm for POT and L_w = 28 nm and L_N = 18 nm for PHT. In this study we used RRHT polymers: relatively long POT (GPC-data: Mw = 142 kg/mol; PDI = 2.6), and shorter PHT (GPC-data: Mw = 24.5 kg/mol; PDI = 1.4).

Aggregation in a good solvent (chloroform). Spin coating of a relatively concentrated PHT solution (0.1g/l) in chloroform results in a smooth film (root mean square (RMS) = 0.6 nm, Figure 2a) with a lamellae morphology that evidently from AFM phase image. Slow evaporation of the solvent from PHT solution at lower polymer concentration (0.02 g/l) leads to a lamellar network about 2 nm in the height (H) (Figures 2b, d). Elongated domains (H = 2-4 nm and L = 30-50 nm) form at slow evaporation of the solvent from extremely diluted solution of PHT (0.001g/l) (Figures 2e, c). Even longer structures (length up to 120nm) are formed at the same conditions from the solution of higher molecular weight POT (not shown). Such an observation

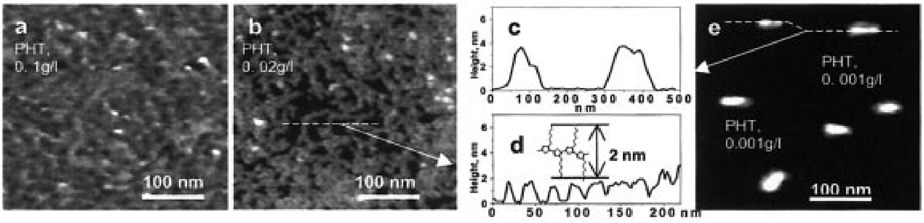

Figure 2. AFM phase (a), topography (b, e), images and cross-sections of PHT (c, d) deposited from CHCl3 solutions at different polymer concentration: 0.1g/l (a); 0.02g/l (b, d); 0.001g/l (c, e).

consistent with the face-to-face aggregation of PATs molecules adopted the rod-like (all-*anti*-) conformation and oriented perpendicularly to the surface (Figure 1a) and is in agreement with previously reported data.[3,14] Red shifted absorption maximum in UV-vis spectra of the PHT film spin-coated onto the quartz slide (λ max = 530 nm and weak shoulder at 600 nm) reflects distinct planarization of the backbone and moderate order of the molecular packing.

Solvatochromism in polar solvent (methanol). It is well-documented that addition of methanol to PATs solution in chloroform affords a colloidal solution.[8] Such a transformation accompanies with a concentration independent bathochromic shift of the π-π* adsorption band from λmax = 450 nm (in chloroform) to λmax = 520 nm with two weak shoulders at 560 and 610 nm (in chloroform-methanol (CM) mixture - 1/1(v/v)) (Figure 3a).

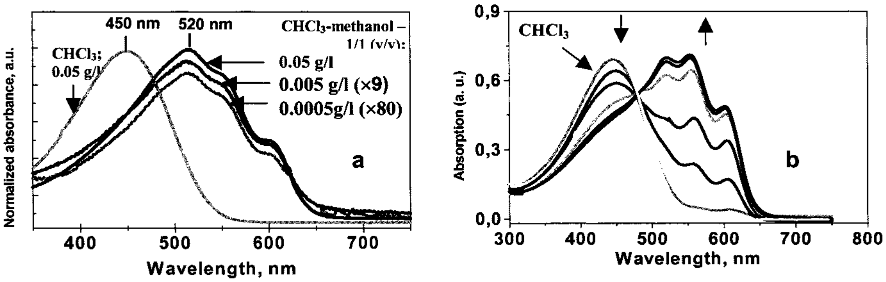

Figure 3. UV-vis spectra of PHT taken in chloroform at concentration 0.05g/l (gray line); taken in chloroform – methanol mixture (1/1(v/v)) at different concentration: 0.05g/l; 0.005g/l (intensity of adsorption have been increased in 9 time); 0.0005g/l (intensity of adsorption have been increased in 80 time) (a); UV-vis spectra of PHT (0.05g/l) at different chloroform-hexane ratio (vertical arrows show evolution of the spectra upon increasing of hexane content)(b).

Figures 4a, b show representative AFM images and cross-sections of adsorbed particles about H=20nm and 100-200nm in diameter (D) formed in CM solution (1/1 v/v) o POT at relatively high polymer concentration (0.015 g/l).

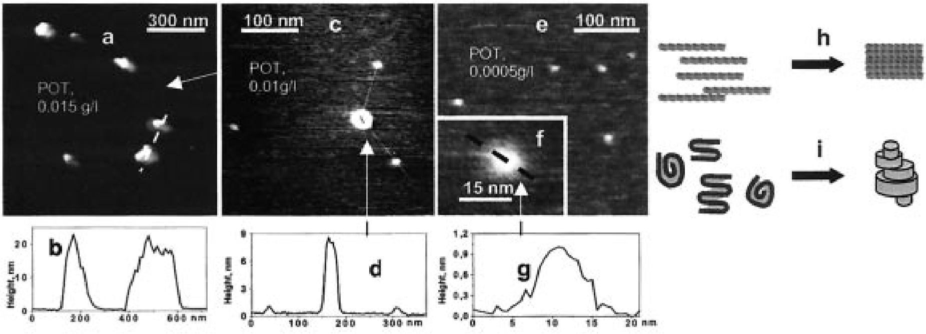

Figure 4. AFM topography images and cross-sections of POT deposited from chloroform-methanol solution (1/1(v/v)) at different polymer concentration: 0.015g/l (a, b); 0.01g/l (c, d); 0.0005g/l (e, f, g); Schematic representation of different aggregation modes of PATs: the face-to-face packing of chains in all-anti conformation (h); aggregation of collapsed hair-pin and spool-like conformations (i).

Diameter of the particles is larger than calculated contour length of POT molecules, therefore, any conformation listed in the Figure 1 from extended to collapsed, in principle, can fit the aggregates in Figure 4a. Deposition from extremely diluted PATs solution (0.0005 g/l, CM mixture - 1/1v/v) immediately after addition of methanol leads to small uniform disk-shaped particles with H = 0.4 - 0.8 nm and D = 15 - 20 nm that correspond to D = 5 - 10 nm after deconvolution (AFM image not shown). Slightly larger particles with the similar morphology were adsorbed from POT solution of the same concentration and solvents composition (apparent values: H = 0.5 - 0.9 nm, D = 25 – 40 nm; diameter after deconvolution D= 10 – 25 nm, Figures 4e, f, g). In both cases length of the particles is considerably less than the calculated contour length of corresponding PAT molecules that displays their *collapse.* The volume of these particles are close to the volume of corresponding PAT molecules that clearly reflects lack of the aggregation at this concentration regime. At a concentration higher than 0.005 g/l PATs molecules start to aggregate. Figures 4c, d display the coexistence of small particles (similar to the one in Figure 4c) and larger aggregates (apparent values: H = 8 – 10 nm; D = 45-65 nm; after deconvolution D = 20 – 40 nm) adsorbed from POT solution (0.01 g/l). On the other hand, *concentration independence* of the UV-vis absorption spectra (Figure 3a) indicates that efficient planarization of the backbone and increase of the conjugation length occurred upon addition of methanol to solution of PATs in chloroform are *single-molecule events*. From obtained experimental data we can conclude that, at least, at low polymer concentration, upon addition of the solvent, which is poor for alkyl side groups, PATs molecules *firstly undergo collapse transition into the compact and planar state and then aggregate.*

Our observation disagrees with the most accepted model for the aggregation of PHT and other substituted polythiophenes occurring in poor solvents. Accordingly with this model, PATs aggregates consist of face-to-face stacked molecules having a *planar rod-like* conformation similarly to the organization of PATs films (Figure 4h).[8] In this case, at least, one dimension of such a particle should be equal (or more) to the contour length of PAT molecules (120-50 nm for POT) that contradict AFM data. As seen from AFM images not only single-molecule particles in Figure 4e but also primary aggregates in Figure 4c have dimensions less than the contour length of POT molecules. Therefore, we proposed that in chloroform-methanol mixture PATs molecules undergo solvophobically driven collapse into the structures with high content of cis-configuration of thiophene units (hair-pin or spool-like conformation, Figures 1b, c). Such conformations reduce a solvent-accessible surface area and decrease an unfavourable interaction between alkyl groups and polar environment. Further aggregation of flat spool-like structures leads to poorly ordered particles (Figure 4i).

It was previously reported[3] that, diffractogram of RR PHT cast films deposited from chloroform has sharp reflections at 2θ = 5.3°; 10.7° and 16.2° which can be assigned to the (100), (200), and (300) planes of a lamellar phase with a spacing 16.7 Å. In that case alkyl chains act as spacers between stacks of closely packed planar main chains. The peak at 23.1° (3.8 Å) corresponds to thiophene face-to-face stacking distance. In contrast, a powder X-ray diffraction pattern of RR PHT precipitated from methanol-chloroform mixture,[8] has considerably less intense peak at 2θ = 5.3°, weak peaks at 10.7°, and 16.2°, and broad galo at 15-25° that reflects *similar but significantly less ordered* molecular packing. Such an observation fits the proposed model of the PHT collapse followed by the aggregation occurred in methanol-chloroform mixture. The spool-like structure shown in Figure 1c presents the PHT molecule with the degree of polymerization (DP) equal to 52. More than half of monomer units of this structure (32 units) have *anti*-configuration and form slightly distorted lamellae with the spacing 16.7 Å. Remaining 20 monomer units in the structure (Figure 1c) adopt syn-conformation and can be responsible for the broad galo centered at 20°. Even higher fraction of anti-configuration and more intense reflection at 5.3° one can expect for PHT molecules of higher DP.

Solvatochromism in unpolar solvents (hexane). Although solvatochromism of PATs induced by polar solvents have been widely studied, their behavior in unpolar solvents is considerably less investigated.[11] High molecular weight PATs are insoluble in hydrocarbons, however, we found that a stable colloidal dispersion could be obtained upon addition of hexane to the solution of PATs in chloroform. This accompanies with considerable red shift of UV-vis absorption maximum from λmax = 448 nm in pure chloroform to λmax = 559 nm (for POT) and λmax = 553 nm (for PHT) in chloroform-hexane - 1/5 mixture. Appearance of the fine vibronic structure (resolved transitions at 522 nm; 559 nm; 605 nm for POT and 520 nm; 553 nm; 602 nm for PHT) indicates the rigidification of the conjugation system. The clear isobestic point at 480 nm (for PHT) reflects a discontinuous character of the transition and the coexistence of two distinct conformational structures for these polymers (Figure 3 b).

Figure 5 shows the AFM images of particles adsorbed onto mica from solution at different PHT concentrations and chloroform-hexane (CH) ratios.

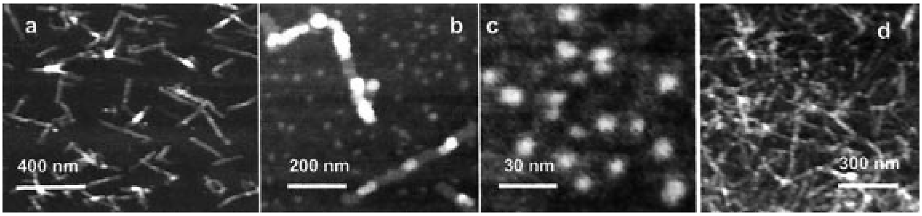

Figure 5. AFM topography images of PHT deposited from chloroform-hexane solution (1/5(v/v)) in 15 minutes after addition of hexane at different polymer concentration: 0.01g/l (a); 0.4g/l (d); immediately after addition of hexane: PHT concentration - 0.01g/l (b, c).

We performed the statistical analysis of geometrical parameters extracted from the AFM images and profiles including number and weight average lengths for one-dimensional (1D) structures, as well as diameter and height for spherical particles. Narrow distributed round-shaped particles with D = 3-5 nm and H = 1-2.5 nm (all data given after deconvolution) were adsorbed from the PHT solution at concentration 0.001 g/l and CH ratio - 1/5(v/v), which had been stirred during 15 minutes before deposition (not shown). Adsorption onto mica from the solution of POT at the same conditions resulted in particles with H = 2-10 nm and D = 3-5 nm (not shown). At higher polymer concentration (0.01 g/l) PHT molecules exhibited selective 1D growth into rod-like structures with the length up to 700 nm (Figure 5a). In contrast, adsorption from PHT solution of the same concentration (0.02 g/l) immediately after addition of hexane resulted in coexistence of small particles (H = 1.0-2.0 nm; D = 3-5 nm) and 1D aggregates (L > 200 nm, Figures 5b, c). Such a picture is an obvious evidence for a non-equilibrium state of the aggregation process. Spin-coating of a relatively concentrated solution of PHT (0.4 g/l) in chloroform-hexane mixture (1/5) leaded to well-distinguished network of rod-like structures (RMS = 4.6nm, Figure 5d). Well resolved UV-vis spectra of the PHT film deposited onto the quartz slide from chloroform-hexane mixture (1/5) (λmax = 523, 556, and 601 nm) differed considerably from the spectra of PHT film obtained by spin-coating from chloroform solution and closes to those taken in chloroform-hexane mixture (1/5). Obtained results show that there is no significant altering of solution conformation of PATs molecules during adsorption and solvent evaporation. Thus, in the chloroform-hexane mixture PATs undergo conformational transition from random twisted into a more planar and ordered state followed by the 1D-aggregation. Two following possible mechanisms for such transformations including a formation of rod-like micelles and the helical conformation have been recently proposed and discussed in our previous paper.[11]

Conclusion

Diverse conformational transitions and aggregations of RRHT PATs in different environments have been studied by means of AFM and UV-vis-spectroscopy. Aggregation from chloroform solution which is a good solvent for PATs, occurred upon slow evaporation of the solvent leads either to the lamellar network or to the elongated domain structures depending on polymer concentration. Red shifted and poorly resolved electron absorption spectra of PHT thin films reflect distinct planarization of the backbone and moderate order of molecular packing. Such observations consistent with the face-to-face packing mode of PATs molecules adopted the rod-like (all-*anti-*) conformation. In presence of methanol, which is *non-solvent* for both alkyl side groups and aromatic backbone at *low polymer concentration*, PATs chains fold into compact poorly ordered flat structures without aggregation. Concentration-independent UV-vis spectra confirm single molecule origin of solvatochromism of PATs. At higher polymer concentrations PATs molecules undergo 3D aggregation into near spherical particles. In hexane, which is the *selective solvent* for alkyl side chains, PATs molecules undergo *ordered main-chain collapse* followed by 1D aggregation. The *concentration-independent* red shift of λmax and good resolved fine vibronic structure in the electronic absorption spectra indicate that planarization occurs on the *single-molecule level*. The *helical conformation* of the main chain of PATs with twelve thiophenes rings per each helical turn has been proposed.[11]

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