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Side Chain vs Main Chain. Who Dominates? A Polyester-Grafted Poly(*p*-phenyleneethynylene) with Two Different Morphologies

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Self-assembly of polymeric chains, a critical aspect in macromolecular materials, is reflected in their morphology. The structure and morphology of macromolecular assemblies at solid interfaces dictates the performance of optoelectronic devices such as organic light-emitting diodes, thin film transistors, and photovoltaic cells.[1−3] Association processes are extended in biocompatible macromolecules, at the interface with membranes, leading to polymer-mediated stabilization of micelles and vesicles, which have great potential in drug delivery and gene transfection.[4−6]

While nature handles the fabrication of well-defined macromolecules that exhibit highly hierarchic structures with ease and elegance, synthetic polymeric systems have a harder time to emulate the size control, function, and monodispersity of naturally occurring species. The association of synthetic polymers has been studied predominantly in block copolymers of narrow polydispersity; the segregation of incompatible components and their differential interaction with solvents results in a rich variety of well-defined micellar structures.[7]

Different assemblies are found in nature, where large, structurally controlled species are prevalent. Among the unique polymer morphologies are linear bundles[8−10] and circular assemblies,[11] found in biological macromolecules and in ionic polymers. The primary building blocks, already displaying a complex structure, associate further into large distinct clusters. Such clusters are formed by both mono- and polydisperse polymers where their size is controlled by an exquisite interplay of electrostatic, hydrophilic, and hydrophobic forces. The factors responsible for the gestation of large, well-defined structures in polydisperse species remain open. The implications of hierarchic ordering in synthetic polymers in general and their effects specifically on the function of conjugated polymers are also unclear, yet important.

In the present study we demonstrate two well-defined mesoscopic structures formed by a polydisperse polyester-substituted poly(*p*-phenyleneethynylene) (PPE **5**). Aggregates of **5** appear in the AFM images as *monodisperse* spherical−circular objects that anneal at elevated temperatures into elongated needlelike bundles. The structure and the size of the observed features are governed by the interplay between the stacking of the backbone and the association of the side chains.

The interaction between PPE chains results in a variety of structures from long-range liquid crystalline correlations[12] to micrometer sized, well-defined strands at the interface with SiO_x.[13] To explore the effects of the interplay between the side chains and the backbone on the association modes of PPEs, we prepared the partially polyester-substituted PPEs **5**−**7**. Here we report the supramolecular assemblies of **5** when cast from solutions onto silicon oxide wafers and follow their morphological evolution with annealing into a thermodynamically stable state.

The building block **1** was reacted with 20 equiv of caprolactone **2** in the presence of tin(bisoctanoate) to give the macromonomer **3** in quantitative yield.[14] A 1:9 molar mixture of **3** and **4** was reacted with acetylene gas in the presence of $(Ph_3P)_2PdCl_2$ and copper iodide in piperidine and THF as solvents. The deep yellow and flaky polymer **5** was isolated in 89% (Scheme 1).[15,16] According to gel permeation chromatography (GPC, polystyrene standards), **5** has a degree of polymerization, P_n, of 86 backbone phenyleneethynylene units ($M_n = 4.6 \times 10^4$) and a polydispersity (PDI) M_w/M_n of 5.6. Polymers **6** and **7** were made by a similar route and display an M_n of 3.7×10^4, a PDI of 3.9 (**6**), and an M_n of 2.6×10^4, with a PDI of 2.9 (**7**).[14] The polydispersity of **5**−**7** is typical for these types of polymers.

Thin films of **5** were obtained by drop-casting onto or dipping silicon wafers into a 0.1 wt % solution of **5** in chloroform. The solvent was allowed to evaporate slowly, and the films were placed in a vacuum (10^{-3} Torr) at room temperature to remove entrapped solvent. Figure 1 shows representative atomic force microscopy images (AFM, tapping mode, TM; Digital Instruments) of **5** as cast and after annealing at 140 °C. With increasing tapping strength, denoted as $1/V_0$, the image changes and structures on multiple length scales appear. Under the lowest tapping strength (Figure 1a) where a clear image is recorded, the film of **5** consists of spherical assemblies with a characteristic size of 30−40 nm. Upon increasing the tapping strength (Figure 1b), unique, ring-shaped features appear and persist across the films. The images are reversible as a function of tapping strength and the phase mode follows the height. Increasing the tapping strength reveals buried structures, observed as bright features in the image. Traces of the height across the features (SI) show that the center of the rings coincides with the widths at half-maximum of the spherical aggregates.

When pristine films of **5** were annealed for 15 min at 140 °C (Figure 1c), the prevalent spherical structures, visible as nanoscale rings at high tapping strengths, have disappeared and ca. 17 nm wide, needlelike features appear. These are visible at any tapping strength and characteristic of features of homogeneous density. Images recorded after 2 and 5 min of annealing reveal intermediate stages of coexisting spheres and needlelike morphologies, affirming that none of the morphologies are induced by the AFM probe.

Surprisingly, the size distributions of both the spherical and the elongated assemblies are narrow. An examination of polymer chains of **5** (from GPC measurements) indicates that the average chain has dimensions of 55 × 17 × 0.4 nm with 55 nm being the extended backbone length, 17 nm the width of the fully extended polyester side chains, and 0.4 nm being the thickness of the chains. According to elementary geometry, the observed circle with a diameter of 33 nm has a circumference of 104 nm, double the average length of a single chain of **5**. Height profiles (SI) indicate that the average aggregate is 0.6−0.8 nm thick and 14 nm wide.

The formation of spherical aggregates requires bending of the semirigid PPE backbone This bending is induced by the large side-chain substituents. Depending on molecular weights

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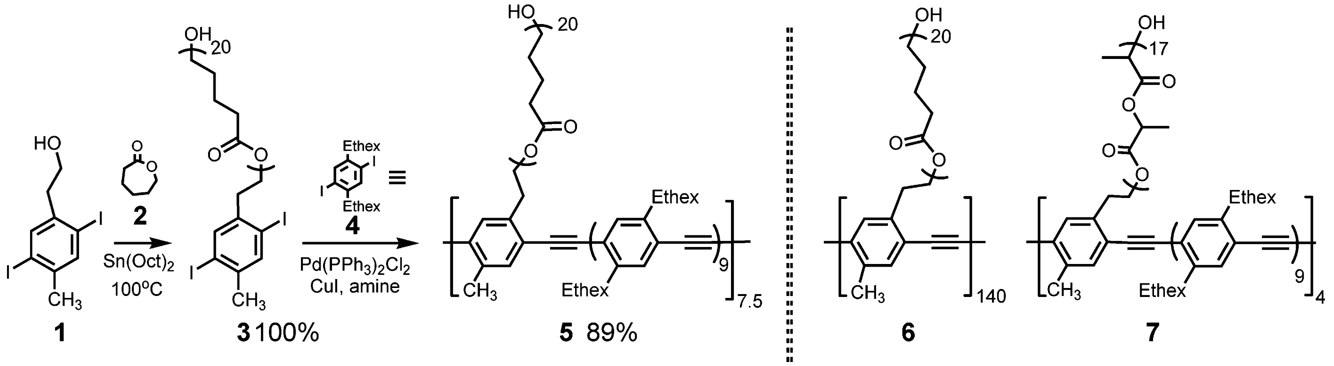
Scheme 1. Synthesis of the Polymer 5 and Structural Formulas of Polymers 6 and 7 (Ethex = 2-Ethylhexyl)



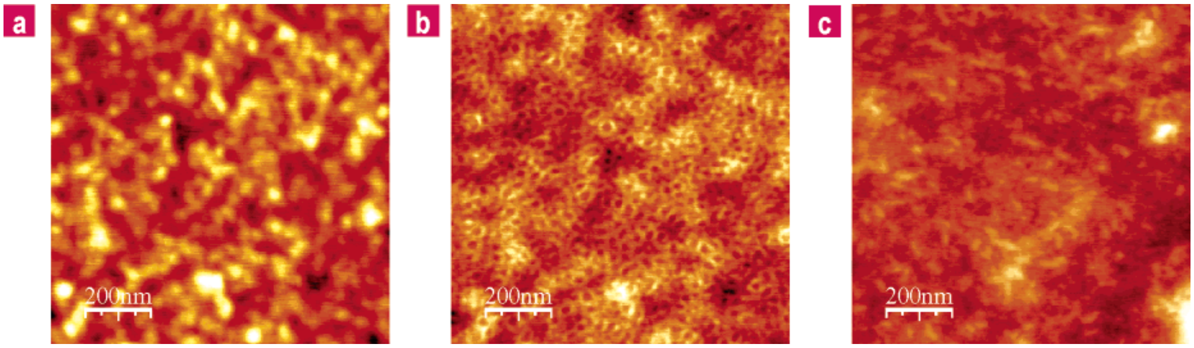


Figure 1. AFM topography images of a drop-cast thin film of **5**, following the evaporation of the solvent and after annealing. (a) Pristine film. Light tapping strength at a set point $V_0 = 1.69$ V. Only surface topology is visible. (b) Same film observed at a higher tapping strength ($V_0 = 1.23$ V). (c) Same film as in (a) and (b) but after annealing to 140 °C for 15 min, recorded at a tapping strength $V_0 = 0.98$ V.

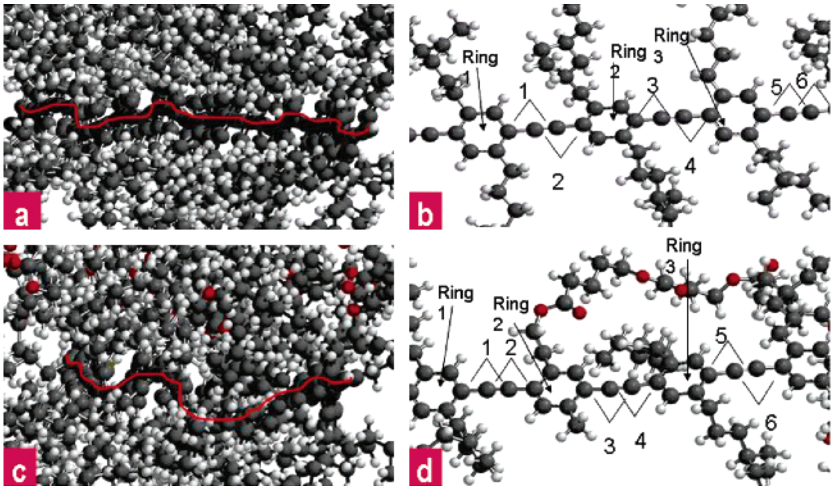


Figure 2. Lowest energy configuration of a single molecule of bis(ethylehexyl)-PPE (top row) and of **5** (5 polyester side chains, 10 repeats for each, 44 phenyleneethynylene units on the backbone) (bottom row) obtained by SPARTAN 04 using a molecular mechanics model with the MMFF force field. In the images, the black spheres, the white spheres, and the red spheres represent carbon atoms, hydrogen atoms, and oxygen atoms, respectively. The red lines indicate the trend of backbone. (a) No polyester (PE) side chain attached. The bending angle between a single C−C bond and the triple bond is calculated to be 178 ± 1°. (b) Details of the backbone. (c) PE side chain attached. (d**)** Detailed view of a PPE with a PE with side chain attached; CCC bond angles between C−C-single and C−C-triple bonds: 1, 178.2°; 2, 178.2°; 3, 174.2°; 4, 175.0°; 5, 176.0°; 6, 176.5°.

and the nature of the substituting groups, PPEs are semiflexible and wormlike or more rodlike when aggregated.[17−23] To shape a 75-meric phenyleneethynylene into a half circle, each PE unit has to bend by 2.4°, a very slight distortion; circular PPEs with less than 12 repeat units have been made and are stable.[24] The formation of self-assembled circles is corroborated by the molecular mechanics calculations of the minimum-energy conformation of a single chain of **5** (vacuum, no solvent, Figure 2), demonstrating that at the substitution site of the polyester the conjugated backbone has an increased propensity to bend; circular or semicircular arrangements are plausible. A deviation of up to 7° is calculated in the phenylenalkynylene units adjacent to the sites of the grafted polyester, while further away (Figure 2) the aryleneethynylene units are close to linear.

While it is feasible to obtain circular aggregates by a slight change of the chain geometry, these are not the thermodynamic stable state of the system. The interaction of the backbone and the different side chains with the solvent are among the driving forces that result in the formation of the spheres.[4] Upon heating to 140 °C, the spheres form clusters of well-defined size. At this temperature, both the side chains and the backbone, are above their glass transition temperature, 50 ± 5 and 111 ± 10 °C, measured for side chains and the backbone respectively by DSC in bulk samples. Heating **5** above the glass transition

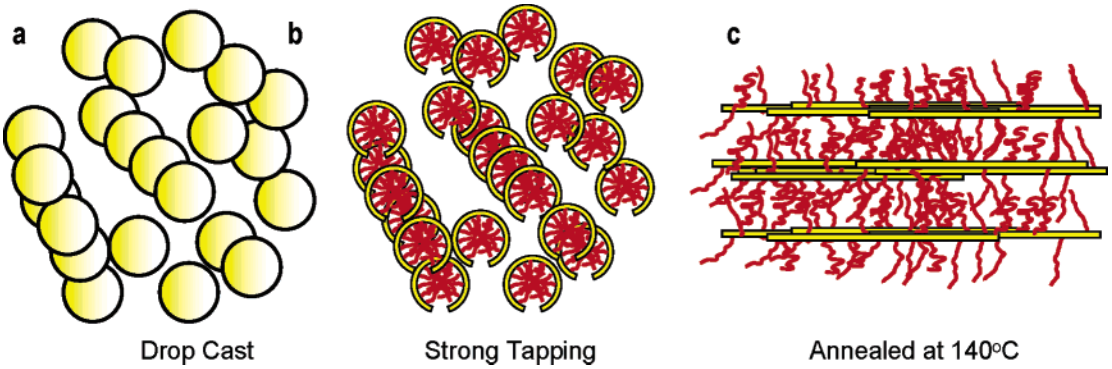


Figure 3. A schematic model of the morphology development of the polyester-substituted PPEs **5**. (a) Pristine film drop cast from solution; light tapping. (b) Rings formed by the backbone are revealed by AFM under strong tapping conditions. (c) Upon heating to 140 °C the locally phase separated morphology relaxes into the global minimum, a stranded PPE phase.

temperature of both segments allows rearrangements to a thermodynamic stable state dominated by the interaction of the backbone and the side chains that is mediated by the interfacial interactions. Figure 3 proposes a mechanism for the gestation of the different association modes. Under nonequilibrium conditions, the polyester side chains of **5** aggregate locally. In the spheres, approximately 30 polyester chains fill the interior, forcing the PPE main chain to bend to its spatial needs; upon heating the PPE chains relax.

The uniform size of the spherical aggregates suggests that the self-sorting process works efficiently because we observe features of the same size (33 nm) in different samples. The optimum filling of the interior of the features by the hydrophilic side chains force the backbones into the spherical morphologies. The spheres may be formed by any number of chains of **5**, balancing the association energy of the hydrophilic segments with the elasticity of the main chain and its intrinsic propensity to aggregate. The actual number of PPE chains involved in the formation of one sphere cannot be resolved due to the high polydispersity of **5**.

Different types of aggregates have been observed in di- and triblock copolymer solutions, including spherical and cylindrical micelles as well as vesicles.[7] As the solvents evaporate, larger structures such as polydisperse tori that consist of numerous molecules were observed by Pochan et al.[4] Discrete clusters (tetramers, etc.) have been described by Müllen and others[25,26] upon evaporation of solvent from dilute solutions of dendrimers. However, the formation of discrete small aggregates in PPEs or similar conjugated polymers is unprecedented. Upon drop-casting, dipping, or spin-casting of solutions of **6** or **7** with a similar chemical structure only stranded or needle-like aggregates were visible. The absence of a vesicular phase in **7** may be due to the lesser degree of polymerization of its main chain or to the enhanced rigidity of the polylactide side chain.

In conclusion, we report the self-assembly of a polyester-grafted PPE **5** into a spherical morphology. In this solvent-induced, kinetically trapped, but thermodynamically unstable state, the side chains dictate the morphology, while in the annealed, relaxed phase the main chains dominate the association; a stranded, needlelike phase is formed. The answer to the question posed in the title is, “it depends”. In annealed films, in the thermodynamic equilibrium, the main chains control the morphology, while in the kinetically trapped solution state of **5**, the side chains force the main chains into soft spheres that appear as circles when probed by AFM using high tapping strengths.

Ongoing work to resolve the effects of molecular weight, concentration, and tacticity of the side chains is aimed at determining the conditions under which the PPE backbone is perturbed to the extent that will allow control over the bending of the chains. These characteristics will offer a means to control the association and the electrooptical characteristics of PPEs in the solid state. Additionally we will investigate a number of other solvents and report the results. The ideal solvent for the formation of spheres needs to be able to dissolve the hydrophobic part of the molecule sufficiently. As a consequence, while pentane and hexane would clearly force the polar side chains into aggregation, they do not have sufficient solubilizing power to keep the main chain in solution. As a consequence, dichloromethane and chloroform may be the perfect solvents to form this type of spherical morphology.

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Supporting Information Available: Preparation of the polymers **5**−**7** and experimental details for the microscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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