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Nanostructure of self-assembled rod-coil block copolymer films for photovoltaic applications

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Abstract

The nanostructures of a series of rod–coil block copolymers, designed for photovoltaic applications, are studied by atomic force microscopy and transmission electron microscopy. The copolymers are composed of a semiconducting poly-*p*-phenylenevinylene rod with (2′-ethyl)-hexyloxy side chains and a functionalized coil block of various length and flexibility. Both, as deposited and annealed block copolymer films were investigated.

The results show that highly ordered structures are only obtained if the coil block is characterized by a glass transition temperature which is significantly lower than the melting temperature of the alkyl side chains. For this material a high molecular mobility and strong driving force for crystallization of the rigid block can be achieved simultaneously. For the smallest coil to rod length ratio, we found a lamellar morphology with perpendicularly oriented lamellae with respect to the substrate. Electron diffraction data show the presence of a periodical molecular arrangement with a characteristic distance of 0.94 nm that is attributed to the distance between conjugated chains separated by the layers of alkyl sidechains.
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Keywords: Rod-coil block copolymer; Organic solar cell; Self-assembled nanostructure; Atomic force microscopy; Transmission electron microscopy

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1. Introduction

In organic photovoltaic devices, the nanoscale morphology of the light harvesting thin film is of fundamental importance. This is particularly true for bulk heterojunction solar cells, where the interface area between electron–donor and electron–acceptor interpenetrating domains plays a key role in the generation of free carriers. High photocurrents are reached only if the domain size is, in at least one dimension, comparable to the exciton diffusion length, and if the intradomain molecular arrangement induces high free carrier mobilities [1]. The bulk heterojunctions most investigated at present are based on blends of donor and acceptor molecules, such as poly(*p*-phenylenevinylene) (PPV) and fullerene derivatives. In these devices, the active layer is commonly in a non-equilibrium state and has a morphology that depends strongly on the deposition process. Moreover, during low temperature annealing, separation of donor and acceptor elements may occur, leading to larger domain sizes and correspondingly lower photovoltaic efficiencies [2,3].

A better control over the morphology and a higher thermal stability can in principle be reached if diblock copolymers composed of two covalently connected polymers (or blocks) with appropriate electrochemical properties are used instead of blends [2–4]. If the two blocks possess sufficient repulsive energy, they will microphase-separate, producing microdomains rich in one block or the other. The resulting morphology is largely determined by the relative block lengths and may consist of spheres, cylinders or lamellae, with domain cross-sections of the order of the block length [5]. In the case of lamellae or cylinders with a dominant vertical orientation, the morphology is close to that of an ideal bulk heterojunction solar cell. In addition, since microphase separation is preserved under equilibrium conditions, the diblock copolymer films have an improved thermal stability in comparison to blends.

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Self-assembled photovoltaic devices making use of rod–coil diblock copolymers consisting of a PPV based semiconducting polymer as the rigid block and a polystyrene chain functionalized with fullerene moieties as the flexible block have been previously studied [4,6]. Strong luminescence quenching and higher photocurrents than in blends of both blocks were obtained and attributed to an enhanced donor–acceptor interface with efficient charge transfer statistics. Despite this encouraging data, the energy conversion efficiencies reported so far for block copolymer devices remain below the typical values obtained for blends [6,7]. Absence of a bi-continuous donor–acceptor network and correspondingly low free carrier mobilities is one of the possible reasons that may cause limited performance. In previously reported devices [4,6], the diblock copolymer layers were indeed obtained by spin-coating without further high temperature treatment, leading presumably to an inappropriate non-equilibrium disordered morphology.

To improve the photovoltaic conversion efficiency of diblock copolymer cells, the microphase separation kinetics during film deposition and subsequent heat treatment needs to be investigated. This is particularly true for rod–coil diblock copolymers, where the equilibrium phase diagram, which describes supramolecular ordering versus molecular structure, is still poorly understood [8,9]. In addition, special emphasis needs to be placed on the relationship between charge transport and molecular ordering. In this article, we report atomic force microscopy and transmission electron microscopy investigations of the supramolecular structure of a series of rod–coil diblock copolymers in spin-coated films as a function of thermal annealing. Coil blocks with two different glass transition temperatures and lengths are used and allow us to investigate the influence of coil flexibility and block length ratio on the self-assembling process. Homopolymer thin films of the rigid conjugated block were also considered for comparison. Using this approach, we aim to obtain a better insight into the experimental conditions necessary to form a supramolecular structure that is appropriate for photovoltaic devices.

2. Experimental details

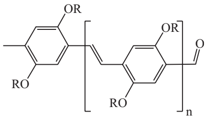
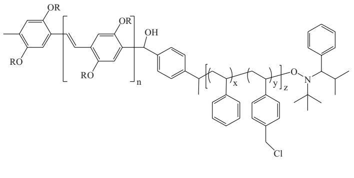
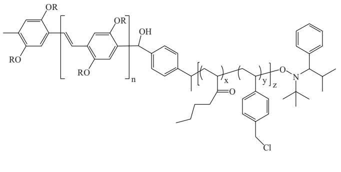
Molecular structure and thermal properties of the materials used for the present study are summarized in Table 1. For the conjugated rigid block we used a 2,5-di(2′-ethyl)hexyloxy poly(p-phenylenevinylene) (DEH-PPV) of low molecular weight (M_n = 4000 g/Mol). DEH-PPV is a hairy mesogenic PPV derivative with low polydispersity (<1.2) that exhibits a liquid crystal behaviour between 65 and 200 °C [10]. It has a molecular geometry that should allow strong π stacking of the conjugated backbone in the solid state, a property that is essential for achieving good charge transport properties.

For the coil block, we used a statistical copolymer of either styrene (ST) or butylacrylate (BA) and 4-chloromethylstyrene (CMS). The molar fraction of CMS was fixed to 8% for BA and to 25% for ST. The presence of CMS gives us the opportunity to attach a controlled amount of C_{60} moieties onto the coil block, when the material is to be used in bulk heterojunction solar cells. Two different lengths of the BA related copolymer were investigated. Both ST and BA related coil blocks differ significantly in flexibility, as revealed by their respective glass transition temperatures.

For the synthesis of the diblock copolymers we used a controlled radical polymerization technique. A detailed description of this method lies beyond the scope of this article and can be found elsewhere [6,11,12].

Thin films were deposited by spin coating of a diluted chloroform solution (between 1 and 2 wt.%) onto silicon substrates under a nitrogen atmosphere (inside a glovebox) at a rotational speed between 1200 and 3000 rpm. The resulting film thickness was between 60 and 200 nm. The solution was stirred at room temperature for at least 24 h and filtered with a 0.2 μm PTFE filter prior to film deposition. Since chloroform is a good solvent for both blocks, aggregation in solution was minimized. The samples were stored under high vacuum for several hours to remove residual solvents prior to structural characterization. Subsequent sample annealing was performed using a temperature controlled hot stage in a nitrogen atmosphere.

Table 1
Physical properties of the polymers used in the present study

	DEH-PPV	(DEH-PPV)-*b*-PS	(DEH-PPV)-*b*-PBA "*s*"	(DEH-PPV)-*b*-PBA-"*l*"
Molecular weight (g/mol)	4000	18 800	6800	16 000
Phase transition temperatures (°C)	T_s: 65 $T_{LC\rightarrow I}$: 200	T_s: 90 $T_{LC\rightarrow I}$: 210	T_s: 85 $T_{LC\rightarrow I}$: 175	T_s: 65 $T_{LC\rightarrow I}$: 170
Coil block glass transition temperature (°C)	–	T_g: 85	T_g: −35	T_g: −35
% coil (wt)	–	58.5	41.2	75
CMS: ST or BA molar ratio	–	1:3	1:11	1:11
Molecular structure	 R = ethyl-hexyl			

The transition temperature T_s is attributed to the melting of the alkyl side chains. $T_{LC\rightarrow I}$ corresponds to the transition into the isotropic state [9].