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Feature Article

Polymer compatibilized self-assembling perylene derivatives

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ABSTRACT

Solution coating of functional small molecules in polymer films is a convenient approach to fabricating flexible optoelectronic and photo-functional devices. Uniform dispersion of the small molecule in the polymer and inhibition of aggregation are requirements for the robust functioning of the devices. Alternate approaches such as incorporating the functional molecule as part of the polymer chain have been examined, although such methods limit the flexibility in materials choice. While perylene or perylene tetracarboxy diimide (PTCDI) or perylene imide (PI) phase separate into discrete crystals in polymer films, we find that functionalizing the perylene imide with a polymer or oligomer segment that is compatible with the host polymer matrix results in highly uniform dispersion of the small molecule, with the inherent photophysical properties of the perylene segment unaffected. We demonstrate this approach with oligostyrene–PTCDI–oligostyrene dispersed in polystyrene, PDMS–PI and PDMS–PTCDI–PDMS in PDMS in solution cast films and in two-component gels from organic solvents. Fluorescent gels of polystyrene and PDMS (without crosslinks or functionalization) were obtained via this route.

Contents

1. Introduction

Dispersing functional small molecules in polymer matrices is a common approach to fabricating organic-based

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flexible devices, the earliest examples being the reprographic photoreceptors and polymer-dispersed liquid crystal displays [1–6]. Solution coating of functional multilayers using such compositions are preferred for flexible devices. The relative concentration of the functional molecule often has to be as high as 50 wt% in the polymer. For example, Santerre et al. [7] reported the properties of OLED devices based on N,N′-diphenyl-N,N′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) dispersed in polymers with high T_g. The best performance was obtained with a TPD concentration of 75%. Detailed studies have been reported on the morphologies resulting from phase separation of three different charge transport molecules in polycarbonates and polystyrene [8–11]. Molecular dispersion of the small molecule is essential and any phase separation and crystallization would lead to degradation of the device performance. Smith et al. [12] have shown that crystallization of TPD was the cause of delamination of an OLED device. Scharfe [13] discussed the effect of such crystallization on charge trapping in photoreceptors. The leaching of the transport molecule would be more prevalent in copiers and printers using liquid developers.

As an alternate to dispersing the functional small molecule in polymer matrices, Limburg et al. [14] and Ong et al. [15] designed arylamine based polymers and copolymers by incorporating the photoactive molecules as part of the chain to prevent phase separation. Design and properties of several such polymers with arylamine functionality in the main chain or side chain have been studied [16–18]. Conjugated polymers for solar cell applications have also been examined [19,20]. All-polymer bulk hetero-junction solar cells using blends of polymers bearing donor and acceptor moieties have been reported by Jenekhe et al. [21]. The advantage of using a functional molecule dispersion in a host polymer is that either can be changed at will, whereas a specific polymer with the functional segment cannot.

Perylene and its derivatives have been investigated over the past few decades for their applications in optoelectronic and photovoltaic devices [22,23]. The classic crystallographic investigations by Hädicke and Gracer [24] related the effect of substituents on the π-overlap and the color. The self-assembly facilitated by the π-interaction can be modulated by substitutions at the imide nitrogen as well as the bay positions [25–27]. Linear and dove-tail substitutions have been used to create nano-fiber morphologies [28,29]. Supramolecular association between melamine functionalized perylene tetracarboxylic diimide (PTCDI) and cyanuric acid via hydrogen bonding resulted in nano-ribbon and nano-rope morphologies [30]. The applications of perylene imides and diimides in solar cell and organic electronics have been summarized in recent reviews [31,32].

When perylene (or PTCDI) by itself was dispersed in a polymer matrix, the small molecule formed discrete crystals of a few microns as shown in Fig. 1, irrespective of the solvent used for casting the films. We discussed the self-assembly of PTCDI substituted with oligostyrene on both imide nitrogens (PS–PTCDI–PS, Scheme 1a) in solution [33] as well as in the gel state [34]. In another study, we substituted poly (dimethyl siloxane) (PDMS) on both imide nitrogens (Di-PDMS) (Scheme 1b) or on one (Mono-PDMS) (Scheme 1c) and reported on the differences in the morphology of the mono and di-substituted PTCDI in solution [35,36] and gels [37]. Both PS–PTCDI–PS and Di-PDMS are non-ionic Gemini surfactants. We believed that by attaching an oligomeric or polymeric chain which is compatible with the host polymer, the mixing of such compatibilized PTCDI would be better, and a uniformly dispersed composite film could be obtained. For example, with oligostyrene attached to PTCDI, we expect that a good dispersion in polystyrene (Scheme 1d) could be achieved. In the present work, we dispersed PS–PTCDI–PS in the corresponding

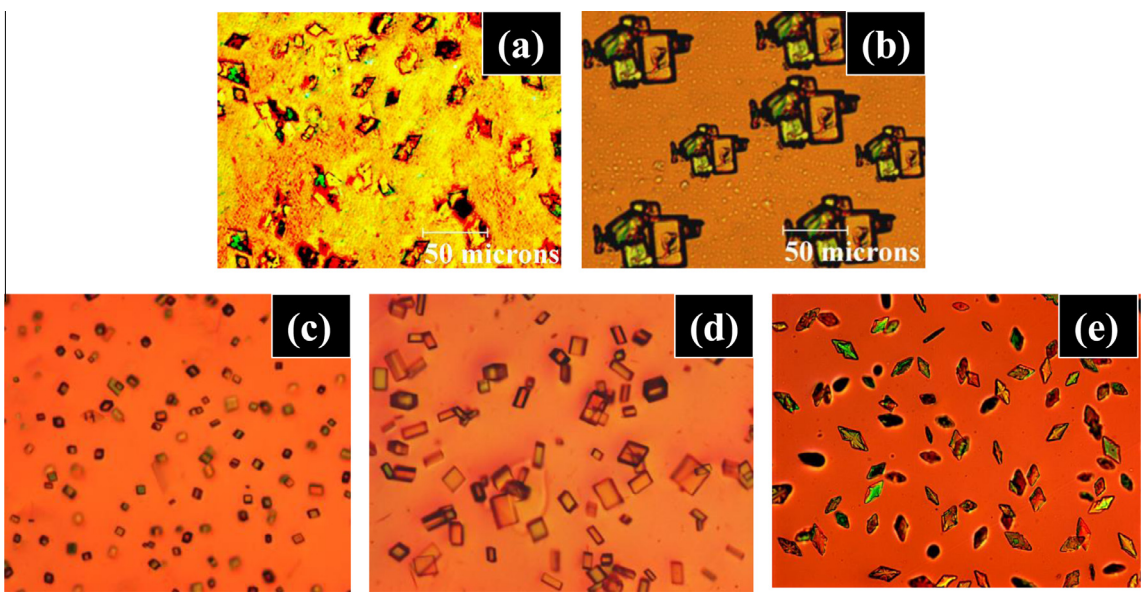

Fig. 1. OM of solvent cast films of (a) perylene/polystyrene (5/95 wt%), (b) PTCDI/polystyrene (5/95), (c) perylene/polycarbonate (2/98), (d) perylene/polycarbonate (5/95) and (e) perylene/PMMA (2/98). Tetrachloroethylene was used for (e) and chloroform for the others.