Pigment-Mediated Nanoweb Morphology of Poly(dimethylsiloxane)-Substituted Perylene Bisimides

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We recently described[1] the micellar and trilayer vesicular morphologies of poly(dimethylsiloxane) end-capped with a perylene unit (PDMS-end-cap-perylene) from nonaqueous media. This was prompted by the studies that have been reported on amphiphilic block copolymer systems, exhibiting micellar or vesicular morphologies depending on the pH of the aqueous system.[2] Essentially, we considered PDMS-end-cap-perylene to be a "block copolymer", in which the degree of polymerization of perylene is one. We expected that these polymers in nonaqueous media would exhibit morphologies similar to those of the amphiphilic block copolymers in aqueous systems. Indeed, depending on whether the solvent was dichloromethane, chloroform, hexane, or mixtures of the chlorinated solvent and hexane, we observed either micellar or a trilayer vesicular morphology. We rationalized these on the basis of the relative solubilities of PDMS and perylene in these solvents. The perylene unit was attached to one end of the PDMS chain in the above work.[1]

The crystal structure and the color of pigments can be manipulated by judicious choice of substituents, as was shown by Hadicke and Graser.[3] Perylene pigments, with short alkyl substituents such as *n*-alkyl perylene diimides (with C_5, C_8, and C_{12} substitution) tend to exhibit liquid crystallinity, and this has been described by Struijk et al.[4] The charge transport kinetics in thin film transistors with these *n*-alkylperylene diimides has been discussed by Chesterfield et al.[5] Balakrishnan et al.[6] discussed the effect of di(dodecyl) and di(nonyldecyl) side-chain substituents on the self-assembly and morphology of perylene diimide molecules. The disposition of the side group with respect to the perylene unit influences the morphology. The possibility of creating nanowires using self-assembled π-conjugated systems was illustrated by Schenning and Meijer.[7]

Here we report an entirely different morphology exhibited by PDMS-perylene bisimide-PDMS, in which the PDMS chain is attached to both sides of the perylene unit, as shown in Scheme 1. We find that due to the stacking of the perylenes and the entanglement of the polymer, a nanoweb morphology is created.

The molecular weight of the PDMS segment used here varies from 900 to 3000. We denote these as D-900, D-1500, and D-3000. The PDMS-end-cap-perylene samples were denoted previously as M-900, M-1500, and M-3000. We synthesized poly(dimethylsiloxane) perylene bisimide (PDMS-perylene bisimide-PDMS) by reaction of perylene 3,4,9,10-tetracarboxylic dianhydride with amino- terminated polysiloxane in *m*-cresol at elevated temperatures. The reaction condition is the same as PDMS-end-cap-perylene, except that perylene 3,4,9,10-tetracarboxylic dianhydride should be slowly added to the solution of amino-terminated polysiloxane, isoquinoline, and *m*-cresol, so that only 2 mol of amino-terminated poly(dimethylsiloxane) reacts with 1 mol of perylene 3,4,9,10-tetracarboxylic dianhydride. The appearance of PDMS perylene bisimide was dark red, similar to PDMS-end cap-perylene.

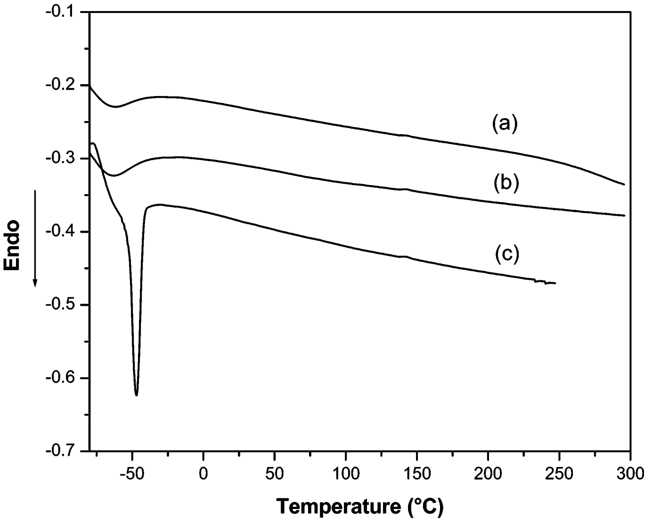

Figure 1. DSC traces for PDMS perylene bisimides: (a) D-900, (b) D-1500, and (c) D-3000.

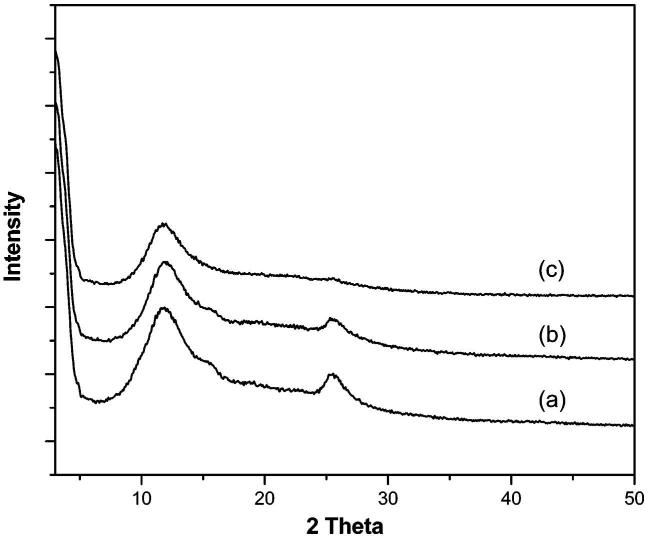

Figure 2. X-ray diffraction of (a) D-900, (b) D-1500, and (c) D-3000.

In the previous study, PDMS-end-cap-perylene showed[1] reversible melting and crystallization transitions, corresponding to the perylene segment, in the DSC. However, the DSC curves in Figure 1 show that PDMS perylene bisimides have no perylene-related melting point or transition temperature. This is similar to the behavior of most perylene bisimides, which melt at temperatures of 300 °C or above their decomposition temperature. Similar to M3000, a melting point at −50 °C is seen for D-3000, which corresponds to the melting of the PDMS segment. In contrast to the perylene diimides with short alkyl substitutents,[4] the PDMS substitution does not lead to liquid crystalline behavior. Thus, it would seem that side chains beyond a certain length do not facilitate the LC behavior. The stability of these compounds is good, with decomposition temperatures (5% weight loss) of 387, 423, and 406 °C for D-900, D-1500, and D-3000, respectively.

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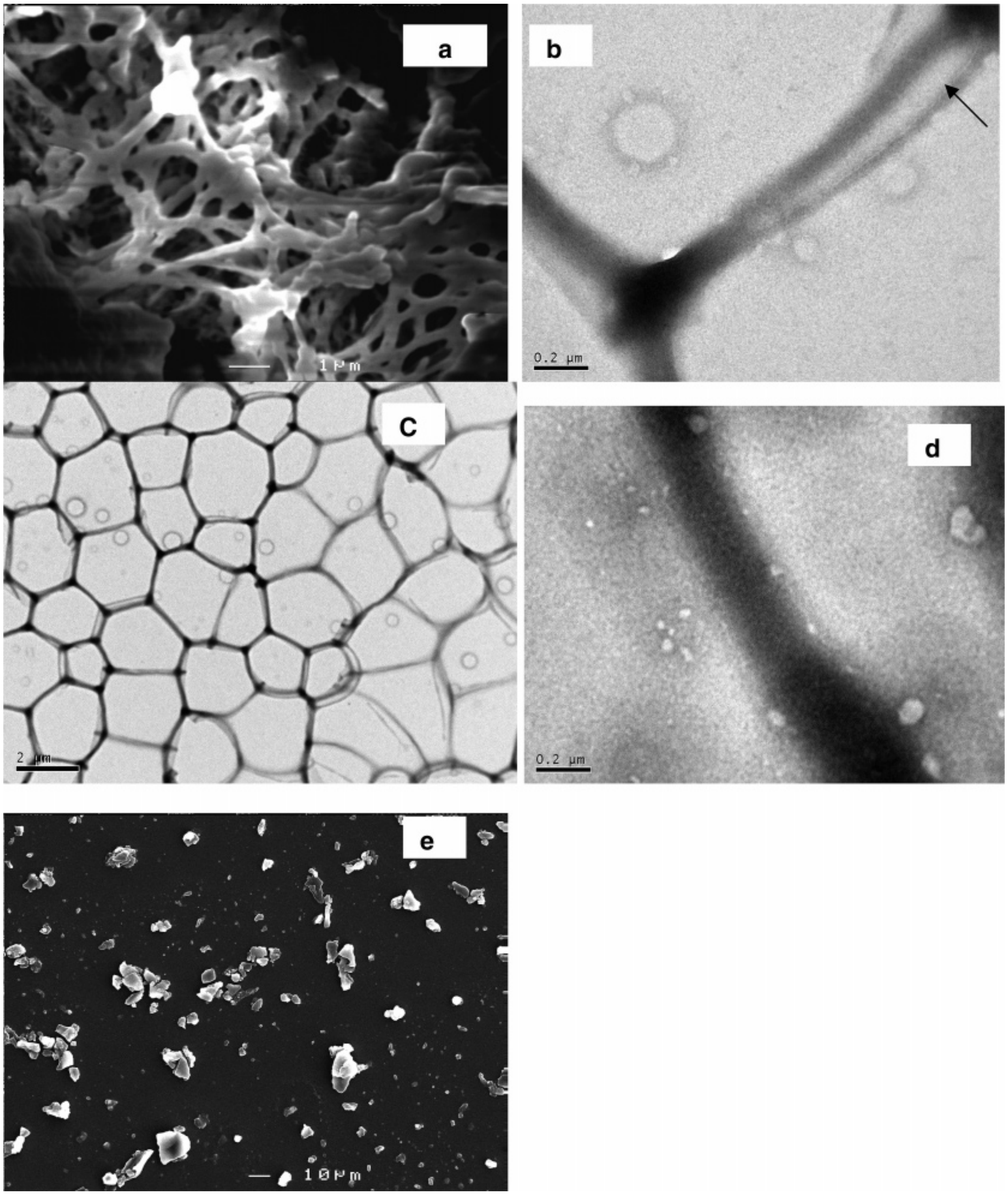
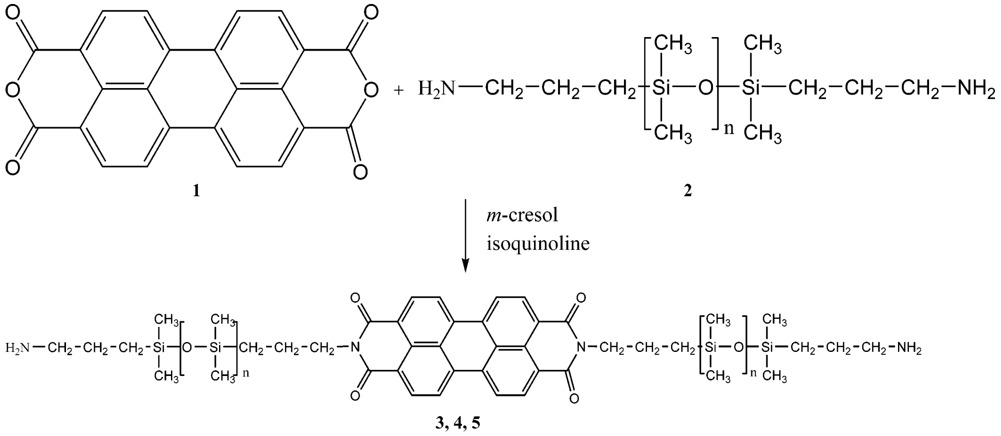
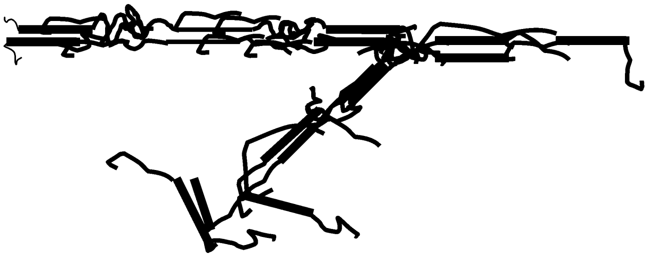


Figure 3. (a) Cryo-SEM of D-900 from $CHCl_3$. (b, c) TEM of D-900 from $CHCl_3$. (d) TEM of D-3000 from $CHCl_3$. (e) SEM of D-900 from hexane.

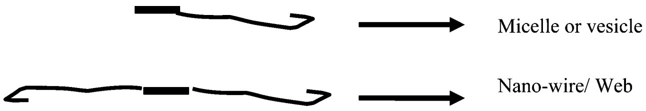
Scheme 1. Synthesis of PDMS Perylene Bisimides: (3) $n \approx 10$ (D-900); (4) $n \approx 20$ (D-1500); (5) $n \approx 40$ (D-3000)



Scheme 2. Schematic of the Wire/Web Formation with π-Stacking and Polymer Entanglement



Scheme 3. Effect of Mono- vs Disubstitution with PDMS on the Resulting Morphology



X-ray diffraction (Figure 2) shows only two broad peaks in Bragg angle intensity which represent spacings of 3.51 and 7.52 Å, corresponding to the face-to-face and the side-to-side packing of the perylenes, respectively. Hence, this system does not exhibit three-dimensional ordering of the perylene units, but a two-dimensional assembly. It is also seen that the relative intensity of the peak corresponding to the 3.51 Å reflection decreases with an increase in the length of the PDMS segment, indicating that the longer PDMS segment impedes the π-stacking.

Figure 3a shows the cryo-SEM of D-900 from $CHCl_3$ solution. The π-stacking of the perylene units, and the entanglement of the PDMS segments, lead to a network morphology. Figures 3b,c show the TEM image of D-900 from $CHCl_3$ solution. The nanoweb morphology is facilitated by the network formation of the wires, which form via such a π-stacking and polymer entanglement, as shown schematically in Scheme 2. In these micrographs, the dark features correspond to electron dense PDMS. The thickness of the wires varies in the network, and the wires are multistranded. For example, in Figure 3b, the thickness of a strand varies from about 3 nm (shown by the arrow) to about 200 nm. The thickness of the PDMS wire increases with its molecular weight, as seen in Figure 3d. Similar to the case of PDMS-end-cap-perylene, the effect of solvent is seen here also. It was noted that the nanowire or nanoweb is not formed with hexane as the solvent. In this case (Figure 3e) particles of the about 10 μm in size are seen, and these can be attributed to the preferred interaction between PDMS and hexane and the PDMS engulfing the perylene units.

While PDMS by itself will not exhibit any structural features at room temperature, the presence and stacking of the perylene units lead to the wire and web morphology. In a unique way, this is a perylene-stack-mediated assembly of the polymer into a nanowire. The partial stacking of the perylene units and the entanglement of the polymer lead to such morphology. In contrast to perylene bisimides substituted with short alkyl chains, the present system does not show liquid crystalline behavior, indicating that the LC behavior is impeded beyond a certain length of the side chain. The crystallinity of the perylene segment is reduced with an increase in the length of the polymer chain. The substitution pattern also leads to significant differences in the morphology, as shown in Scheme 3. Whereas PDMS-end-cap-perylene leads to micellar and vesicular morphologies, PDMS-perylene-PDMS results in a wire−web morphology.

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Supporting Information Available: Synthetic procedure and characterization methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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