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著者(和文)	Wylie Kevin Lawrence
Author(English)	Kevin Lawrence Wylie
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報告番号	甲第	号	学位申請者氏名	Kevin WYLIE		
論文審査 審査員		氏名	職名		氏名	職名
	主査	早川晃鏡	教授	審査員	Martin VACHA	教授
	審査員	安藤慎治	教授			
		芹澤武	教授			
		扇澤敏明	教授			

論文審査の要旨 (2000 字程度)

This dissertation titled “Tailoring the Self-Assembly of Block Copolymers by Functionalizing the Block Interface” focuses on the development of a new molecular design that allows for the arbitrary modification of the interaction parameters (χ) of linear triblock terpolymers. In doing so, the self-assembly behavior can be tailored as desired.

Chapter 1 “General Introduction” outlines the background and state of the art of the field of polymer science and provides context for the results presented herein.

Chapter 2 “Synthesis and Bulk Characteristics of PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers Containing a Short Reactive Middle Block” discusses the synthesis and morphological study of linear triblock terpolymers where the interaction parameters are modified by introducing strongly dissimilar molecules. Poly(styrene-*b*-glycidyl methacrylate-*b*-methyl methacrylate) (PS-*b*-PGMA-*b*-PMMA) is synthesized by living anionic polymerization which affords well characterized triblock terpolymers containing a short middle block of PGMA which was then modified by the base-catalyzed thiol-epoxy ring opening reaction. In doing so, the χ parameters between the inner block and outer blocks (i.e. A/B and B/C) could be modified independently of the volume fractions of each block and the total degree of polymerization. This modification resulted in changes in the self-assembled morphology depending on the relative strength of each of the three χ parameters and included lamellae, hexagonally packed cylinders and tetragonally packed cylinders.

Chapter 3 “Morphological Study of Functionalized PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers Using Simulation” discusses the use of a simulation technique known as self-consistent field theory (SCFT) to investigate the mechanism behind the experimental results observed in Chapter 2. Using a self-made MATLAB program, the self-assembled morphology of each of the polymers discussed in Chapter 2 was simulated and found to match closely with the experimental results. To deepen the understanding of the effect of χ on self-assembly, phase diagrams were constructed by systematically varying χ_{AB} and χ_{BC} at constant χ_{AC} using the same simulation method. This revealed that there is a strong dependence of the self-assembled morphology on the relative magnitudes of the three χ parameters as well as the predicted existence of a previously undiscovered phase for linear triblock terpolymers.

Chapter 4 “Self-Assembly of Side-Chain Liquid Crystal Functionalized PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers” discusses the introduction of liquid-crystalline behavior to PS-*b*-PGMA-*b*-PMMA synthesized in Chapter 2 and its effect on the self-assembled morphology. Using the base-catalyzed thiol-epoxy reaction, a long perfluorinated alkane known to possess liquid crystal properties was introduced to the middle PGMA block. The liquid-crystalline behavior was confirmed experimentally and found to self-assemble into smectic bilayers with a period of about 3.4 nm corresponding to a fully extended head-to-head configuration of the liquid crystal mesogens with little or no overlap. This liquid-crystalline behavior along with the changes in χ determined experimentally had a significant effect on the self-assembled morphology of the triblock terpolymer. In two of the cases, the morphology was found to be an offset double tetragonal array of cylinders with two different length scales which had never been demonstrated for linear triblock terpolymers. A unit cell is proposed and an analysis of the expected x-ray scattering profile is used to confirm the morphology observed experimentally.

Chapter 5 “Synthesis and Bulk Characteristics of Block Copolymers Containing a Functional 1,1-Diphenylethylene Derivative” discusses the limiting case where the degree of polymerization of the middle block is exactly one. Four 1,1-diphenylethylene (DPE) derivatives containing different functional moieties, such as a pendant vinyl bond or tertiary amines, were synthesized via the Wittig reaction and subsequently incorporated into poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) by living anionic polymerization. By taking advantage of the special characteristics of DPE during anionic polymerization, namely its inability to homopolymerize, exactly one functional DPE derivative could be placed precisely at the junction point of the PS and PMMA blocks. The DPE derivatives were then functionalized using an appropriate reaction and the bulk characteristics of the modified polymer were analyzed by small-angle x-ray scattering (SAXS). In one case, when the molecular weight was large, there was a noticeable change in the domain spacing (d) but the underlying cause remains unclear. In another case, using a difunctional DPE derivative and a difunctional small molecule, d more than doubled and the molecular weight was found to have increased significantly, possibly indicating the grafting-through polymerization of the functional PS-*b*-PMMA. In all other cases investigated, there was no significant change in d which was attributed to their low molecular weight.

Chapter 6 “General Conclusion” summarizes the results presented in this dissertation and discusses the future prospects of the research presented here. This work could be extended by transferring the morphologies observed to the thin film regime which presents challenges with respect to the orientation control of the self-assembled morphologies. If successful, this research could lead to applications in microfabrication and organic electronics by combining the directed self-assembly of polymers with the ability to precisely control the interfacial functionality using the methods presented in this dissertation. In short, this paper greatly contributes to engineering and industry. Therefore, this dissertation is considered to be of sufficient value as a doctoral dissertation.

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