A Precise, Rapid, and Robust Method to modify Interfacial Interaction

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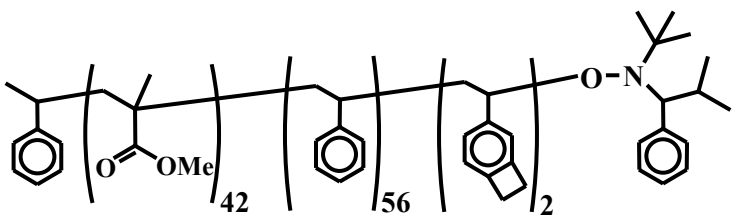
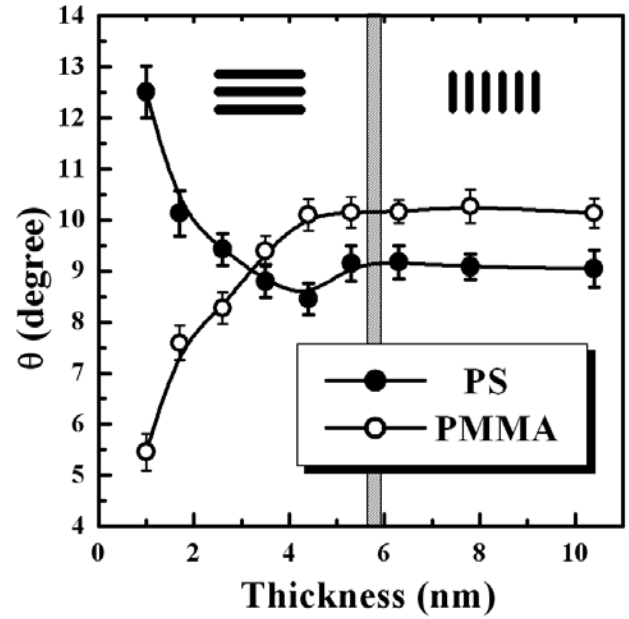
Benzocyclobutene functionalized random copolymers of styrene and methyl methacrylate were synthesized. Thin films of this copolymer, spin coated onto any surface, could be crosslinked within minutes, coating the surface with a robust layer that could be used to manipulate interfacial interactions in a simple, yet precise manner. These crosslinkable films avoids surface specific chemistries required for virtually all other techniques and provides exquisite control of surface energies which is necessary to manipulate the orientation of morphologies in thin films.





Contact angles for PS and PMMA as a function of thickness of a crosslinked BCB random copolymer coating containing 58% S used to modify interfacial interactions. Nanoscopic cylindrical domains of PMMA oriented normal to the surface when the random copolymer layer thickness exceeded ~6 nm as indicated by the schematic morphology diagrams.

The controls of surface and interfacial properties between target matter and substrate have recently drawn attractive attention due to their scientific and practical purposes. These concepts are applicable to soft condensed matters including polymers and biological systems as surface-responsive materials. Consequently, these give rise to a wide range of important phenomena such as tunable surface, surface-directed spinodal decomposition, surface-induced orientation and ordering, mechanically assembled monolayers, molecular chain rearrangement, and the cell behavior on geometrically-patterned surface. In order to get specific response of a target matter at interface, tuning the relative affinities of surface should be required. One of techniques for controlled surface is to build up multicomponent system which is composed of statistically randomly distributed A/B (A-r-B) on the surface with specific interaction. Since it is tunable via controlling of composition of two A and B, there are lots of advantages for applications in surface properties. This strategy was studied in specifically Polystyrene/Poly (methyl methacrylate); (PS/PMMA) system by hydroxyl functionalization to make a linkage between oxide in silicone wafer and end functional group of polymer chains. Although this approach has been used to control the interfacial behavior of polymer blends and block copolymers, the use of hydroxyl functional group has selectively been restricted just for specific substrate which contains matching hydroxyl group.

To overcome this limitation for selectivity of substrate, thus utilize it on any kind of substrate universally, and additionally, take into account of processability as a time problem, the benzocyclobutene (BCB) functionality of new concept is introduced into random copolymer as a crosslinker. Here, we report that well-controlled interfacial properties by statistical random copolymer including BCB can be applied onto any substrate such as Au, Al, Kepton as well as silicon wafer. For their neutrality to the PS and the PMMA at the same time, the composition of random copolymer has been found to be 56/42/2 in mole % as shown in scheme, denoted PS-r-PMMA-r-BCB. In addition, random copolymer prepared by an atomic transfer radical polymerization has molecular weight of 35,000 and a broad molecular weight distribution ~ 1.2. The covalent stabilization can be achieved on the "*crosslinked nano-mat*" since a BCB functional group reacts with a neighbor by crosslinking at higher temperature than 180 oC irreversibly.

The thin film of diblock copolymers have been used due to their self-assembly into well-ordered structure in tens of nanometer scale and applied to their potential uses, such as templates and scaffolds for the fabrication of nano-devices. Surface neutrality on substrates with a certain thickness enables the block copolymers to align with the orientation normal to the substrate avoiding preferential interaction between one of block and substrate. Specifically for such a beautiful template on the neutral brush, asymmetric diblock copolymers composed of PS and PMMA, denoted PS-b-PMMA, have been used to give hexagonally-packed cylinder in thin film.

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Education:

The robust nature of the findings of D. Ryu and E. Drockenmuller (two post doctoral fellows spearheading this research) were underscored by studies. D. Butterfield, an REU participant from Harvard University, used this methodology to manipulate the orientation of cylindrical micro-domain in thin films.

Societal Impact:

The procedure developed to modify the interfacial interactions of any surface has profound implications on the fabrication of polymer-based nanostructured materials and devices. The findings of these interdisciplinary studies can be directly transferred to the manufacturing sector, streamlining and simplifying surface modification processes, and accelerating the processing strategies significantly.