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Thesis Outline

Thesis Title: Studies on the Enhancement of Polymer Structures and Properties by Terminal Functionalization Using Triptycene Units

The structure of polymer assemblies profoundly influences their macroscopic physical properties. Over several decades, efforts to understand and control polymer structuring have intensified, driven by new applications and the development of unique properties. Recently, it has been reported that 1,8- and 1,8,13-substituted triptycenes exhibit a remarkable ability to self-assemble into "2D hexagonal + 1D lamellar" structures, even when incorporated into polymers. This dissertation, entitled "Studies on the Enhancement of Polymer Structures and Properties by Terminal Functionalization Using Triptycene Units", consists of seven chapters. It reports the synthesis, self-assembly behavior, and resulting physical properties of tripodal triptycene terminated polymers. Also, this work presents novel design concepts to enhance the structural and physical properties of polymers using tripodal triptycene motifs.

Chapter 1: "General Introduction". This chapter provides an overview of the historical methodologies related to polymer structuring, emphasizing the micro-phase separation observed in block copolymers, and the self-assembly of polymers terminated with specific structural units. Furthermore, the objectives and the pivotal significance of this research are discussed.

Chapter 2: "Studies on Enantiopure Tripodal Triptycene-Terminated PDMS". Previously studied tripodal triptycene-terminated PDMS containing a mixture of three enantiomers, a consequence of the inherent chirality of the 1,8-substituted triptycene precursor. In this chapter, to understand how the optical resolution of the tripodal triptycene termini influences the assembly behavior and properties of the resulting PDMS, the synthesis and characterization of telechelic PDMS using enantiomers of tripodal triptycenes derived by optical resolution is discussed. The results show that the assembly structure and thermal stability of tripodal triptycene precursors are independent of optical purity. Similarly, an evaluation of the assembly structure and physical properties of the synthesized PDMSs shows that the optical resolution of the triptycene units, when attached to the polymer terminals, has no effect on their assembly behavior and rheological properties.

Chapter 3: "Studies on 1,8,13-Substituted Tripodal Triptycene-Terminated PDMS". In this chapter, experiments to enhance the complex viscosity of PDMS *via* terminal functionalization with 1,8,13-substituted tripodal triptycene having a methoxy group at the 13-position of the triptycene are described. This strategic design is based on the improved thermal stability and structural integrity of 1,8-di(dodecyloxy)-13-methoxy triptycene compared to 1,8-di(dodecyloxy) triptycene. Remarkably, the resulting telechelic PDMS displayed a significantly increased complex viscosity, allowing for the fabrication of free-standing films without chemical crosslinking. Evaluation of the self-assembly behavior and the physical properties of the 1,8,13-substituted tripodal triptycene-terminated PDMS

confirms that mechanical strength is significantly enhanced by the 1D assemblies of PDMS domains between the 2D sheets. This enhancement is attributed more to the 1D PDMS structure than the 2D sheets formed by the assembly of tripodal triptycenes. Another important feature discussed is the self-healing properties exhibited by films derived from this telechelic PDMS.

Chapter 4: "Studies on Narrow-Dispersed Tripodal Triptycene-Terminated PDMS with or without Additive Triptycene". In this chapter, the synthesis, assembly behavior, and physical properties of triptycene-terminated PDMS with narrow molecular weight distributions are described. Surprisingly, triptycene-terminated PDMS with a narrow molecular weight distribution is found to exhibit inferior structuring and mechanical properties compared to telechelic PDMS, with a similar average molecular weight and a broad molecular weight distribution. This suggests that the presence of tripodal triptycene terminated PDMS with low molecular weight promotes polymer structuring. These results inspired the approach of adding tripodal triptycene as an additive. Further experimental results that show the addition of triptycene to PDMS with a narrower molecular weight distribution significantly enhances its structuring and rheological properties are described.

Chapter 5: "Studies on Tripodal Triptycene-Terminated PEGs". Experiments to extend the utility of structuring polymers using tripodal triptycenes are discussed, in which the synthesis, assembly behavior, and hydrogelation of polymers featuring tripodal triptycenes on both termini of polyethylene glycol (PEG), a water-soluble polymer, are studied. It is noteworthy to mention that PEGs terminated with 1,8- and 1,8,13-substituted tripodal triptycenes form hydrogels, where tripodal triptycene units assemble into a 2D assembly. Furthermore, these tripodal triptycene-terminated PEGs exhibit lower critical solution temperature (LCST) behaviors when present in dilute aqueous environments.

Chapter 6: "Studies on Tripodal Triptycene-Containing Di-Block Copolymers". Experiments to understand the effect of terminal functionalization by block segments consisting of tripodal triptycene-containing side chains on long-range structural ordering are described using terminal functionalized poly(butyl acrylate) (PBA)-based diblock copolymers. Their assembly behavior, physical properties, and structure-property relationships are presented. These diblock copolymers assemble to form "2D + 1D" structures, regardless of the triptycene mass ratios. Detailed investigations revealed that a higher concentration of block segments containing tripodal triptycene side chains leads to the formation of more thermally stable structures with improved rheological properties.

Chapter 7: "Conclusion". The findings and perspectives based on this dissertation are summarized.