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Title	Studies on Inclusion Complex of Helical Polymethacrylates
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(800 words)

Biological macromolecules such as proteins and DNA form one-handed helical structures, which influence their functions in living systems. Inspired by the exquisite helical structure, many researchers have been motivated to develop fully synthetic helical polymers with controlled helicity. So far, a large number of helical polymers have been synthesized and utilized as chiral materials because of the one-handed helicity. Another important feature that results from the helical structure is the capability of the polymers to include molecules in the inner helix. Amylose, a natural polysaccharide, is well known to form an inclusion complex with iodine when iodine molecules are encapsulated in the helical cavity of amylose, the so-called "starch-iodide complex." However, an inclusion complex consisting of a synthetic helical polymer as the host is very rare. Recently, it has been reported that syndiotactic poly(methyl methacrylate) (st-PMMA), a stereoregular commodity plastic, can encapsulate fullerenes such as  $C_{60}$  and  $C_{70}$  within its helical cavity to form a crystalline inclusion complex. The author studied the following five areas pertaining to the inclusion complexes of st-PMMA and its derivatives.

[1]  $C_{60}$  is perfectly spherical shaped having 7.1 Å of the diameter, while  $C_{70}$  is elliptical shaped having 7.1 and 7.9 Å of the minor and major axes, respectively. The author found that the helical st-PMMA recognizes the encapsulated fullerene size and changes its helical structure flexibly depending on the size of guest molecules. The helical st-PMMA cavity showed preferential encapsulation of larger fullerenes based on the recognition. The author succeeded in selective separation of higher fullerenes, such as  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$ , from fullerene soot through the preferential encapsulation.

[2] Inclusion complex formation of st-PMMA and polycyclic aromatic hydrocarbons such as anthracene, phenanthrene, pyrene, and perylene were investigated. As a result, it was found that pyrene and phenanthrene are encapsulated into the st-PMMA helical cavity, giving crystalline inclusion complexes. The st-PMMA/pyrene inclusion complex was prepared by mixing in toluene followed by evaporating the solvent and annealing at 160 °C. Molecular modeling of the inclusion complex implied that the encapsulated pyrene molecules are aligned closely in the st-PMMA helix. The st-PMMA/pyrene inclusion complex film containing 10 wt% pyrene showed a fluorescence emission due to a pyrene excimer formed in the st-PMMA helix, confirming 1D alignment of the guest molecules in the st-PMMA helical cavity.

[3]  $C_{60}$  has attracted considerable interest in the field of materials science because of its unique chemical and physical properties. However, the insolubility of  $C_{60}$  in polar organic solvents such as acetonitrile and acetone limits its application. The author found  $C_{60}$  to be soluble in polar solvents when st-PMMA was used as a solubilizing agent;  $C_{60}$  dissolves through inclusion complex formation. The acetonitrile solution of  $C_{60}$  with st-PMMA showed a thermoresponsive phase transition due to the formation and dissociation of the inclusion complex. Transparent st-PMMA films containing  $C_{60}$  prepared by casting an acetonitrile solution of  $C_{60}$  with st-PMMA showed high heat resistance, which resulted from the crystalline structure of the inclusion complex, and absorbed light in the UV-vis region because of the presence of chromophoric  $C_{60}$  molecules.

[4] The author applied the concept of inclusion complex formation between st-PMMA and  $C_{60}$  to control micro structure of polymer alloys. Polymer alloy based on the inclusion complex of st-PMMA and  $C_{60}$ -end-capped polydimethylsiloxane (PDMS- $C_{60}$ ) were prepared. The PDMS- $C_{60}$  was successfully synthesized by mesylation of hydroxyl-terminated PDMS with methanesulfonyl chloride followed by azidation with sodium azide and cycloaddition with  $C_{60}$ . Encapsulation of the PDMS- $C_{60}$  within the st-PMMA helical cavity was observed in toluene as evidenced by UV-vis analysis. Brown color st-PMMA/PDMS- $C_{60}$  inclusion complex film was obtained without macroscopic phase separation by evaporating the solvent, which showed high thermal property owing to the crystalline structure of the inclusion complex.

[5] The author developed a facile synthetic procedure of highly stereoregular polymethacrylates with various ester groups as pendants. Highly syndiotactic and isotactic polymethacrylates were synthesized by esterification of stereoregular poly(methacrylic acid)s prepared by stereospecific anionic polymerization. Esterification reactions using halogenated compounds proceeded smoothly in the presence of 1,8-diazabicyclo-[5.4.0]-7-undecene in dimethyl sulfoxide at room temperature. By performing the esterification reaction in a stepwise manner, highly stereoregular random copolymers were also prepared. The st-copolymers formed novel stereocomplexes with it-PMMA in acetone, as evidenced by differential scanning calorimetry and X-ray measurements.