Solid-state $^{19}$F and $^1$H→$^{19}$F CP/MAS NMR Analysis of Fluoropolymers having Electronic or Optical Functionality.

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Fluorine-containing polymers (fluoropolymers) are widely used in electronics and photonics because most of them exhibit outstanding functionalities such as high ionic conductivity, ferroelectricity, high insulation, low dielectric constants, low refractive indices, and high transparency from ultraviolet to infrared region. However, the characterization of fluoropolymers using solution or solid state NMR have been difficult because of their insolubility in solvents, high melting temperatures, and the strong homonuclear ($^{19}$F↔$^{19}$F) and heteronuclear ($^1$H↔$^{19}$F) dipolar interactions. Recently, the advances in the high-speed magic angle spinning (MAS) and $^1$H→$^{19}$F cross polarization (CP) techniques allow studies on the chemical structures, morphology, and mobility of fluoropolymers at the molecular level. The benefits from the high natural abundance, the large gyromagnetic ratio, and the substantial range of chemical shifts of $^{19}$F nuclei can be effectively utilized by the developments of special probes and various pulse techniques. This paper summarizes the solid-state $^{19}$F MAS NMR studies carried out in Tokyo Tech and Univ. Durham, UK (prof. R.K. Harris) on fluoropolymers exhibiting electronic and/or optical functionality. In particular, the characteristics and benefits of $^{19}$F MAS and $^1$H→$^{19}$F CP/MAS NMR on the analysis of phase structures, morphology, molecular mobility, and spin dynamics will be reported for semi-crystalline and amorphous fluoropolymers, fluoro-elastomers, fluoro-ionomers, VDF-oligomers, and perfluoroalkane/β-cyclodextrin inclusion compounds.


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