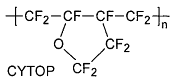
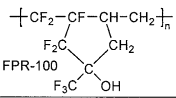
Solid state ^{19}F NMR Characterization of Fluorine-containing Polymers for Electronics and Photonics

Shinji ANDO
Department of Organic and Polymeric Materials, Tokyo Institute of Technology (Tokyo Tech)
Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

Fluorine-containing polymers (fluoropolymers) exhibit unique physical properties, such as high thermal and chemical stability, fire retardancy, low friction, and water-shedding property. In addition, fluoropolymers are widely used in electronics and photonics because some of them exhibit outstanding functionalities of ferroelectricity, high insulation, low dielectric constants, low refractive indices, and high ionic conductivity. However, the characterization of fluoropolymers using solution or solid state NMR have been generally difficult because of their insolubility in solvents, high melting temperatures, and the strong homonuclear (^{19}F↔^{19}F) and heteronuclear (^{19}F↔^{19}F) dipolar interactions. Recently, the advances in the ^{19}F magic angle spinning (MAS) and ^{1}H→^{19}F cross polarization (CP) /MAS techniques allow studies on the chemical structures, morphology, and mobility of fuoropolymers 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 now be effectively utilized by the developments of special probes and various pulse techniques. This paper will describe the characteristics and benefits of ^{19}F NMR and review the solid state ^{19}F NMR studies carried out by the groups of the author (Tokyo Tech) and Prof. R.K. Harris (Univ.Durham, UK) on the phase structures, morphology, molecular mobility, and spin dynamics in the semi-crystalline and amorphous fluoropolymers, fluoro-elastomers, and ionomers as listed in Table 1.

Table 1. Representative fluoropolymers analyzed by solid state ^{19}F NMR

	Partially fluorinated	Perfluorinated
Semi-crystalline Polymer	$-[CF_2-CH_2]_n-$ PVDF	$-[CF_2-CF_2]_n-$ PTFE
	$-[CF_2-CF_2]_n-[CH_2-CH_2]_m-$ ETFE	$-[CF_2-CF_2]_n-[CF(CF_3)-CF_2]_m-$ FEP
	$-[CFCl-CH_2]_n-$ PCTFE	$-[CF_2-CF_2]_n-[CF(OR_f^{a)})-CF_2]_m-$ PFA
Amorphous Polymer	$-[CF(X^{b)})-CF_2]_n-[CH(OR^{c)})-CH_2]_m-$ Lumiflon	 CYTOP
	 FPR-100	
Elastomer	$-[CF_2-CH_2]_n-[CF(CF_3)-CF_2]_m-Z^{d)}-$ Viton	$-[CF_2-CF_2]_n-[CF(OCF_3)-CF_2]_m-Z^{d)}-$ Kalrez
Ionomer		$-[CF_2-CF(OCF_2CF(CF_3)OCF_2CF_2SO_3^-)]_n-[CF_2-CF_2]_m-$ Nafion

a) Perfluoroalkyl group, mainly C_3F_7. b) F or Cl. c) Alkyl groups terminated by H, OH, or COOH. d) Crosslinking point.

Acknowledgement : I thank R.K. Harris, K. Aimi, and H. Tatsuno for measurements and discussions.

References

[1] S. Ando, R. K. Harris, P. Hazendonk and P. Wormald, *Macromol. Rapid Comm.*, **26**, 345-356 (2005).
[2] J.-W. Park, Y.-A. Seo, I. Kim, K. Aimi, S. Ando, and C.-S. Ha, *Macromolecules*, **37**(2), 429-436 (2004).
[3] H. Tatsuno and S. Ando, *Kobunshi-Ronbunshu*, **60**(4), 145-157 (2003).

Correspondence : e-mail sando@polymer.titech.ac.jp; TEL +81-3-5734-2137; FAX +81-3-5734-2889