Variable-temperature $^{19}$F MAS and $^{1}$H→$^{19}$F CP/MAS NMR spectra (spinning at 16 kHz) have been measured for a vinylidene fluoride and trifluoroethylene copolymer, P(VDF$_{75}$/TrFE$_{25}$) (Daikin, Japan), which exhibits a ferroelectric↔paraelectric phase transition. The changes in the local conformations and molecular mobility accompanied with the phase transition were investigated.

Fig.1(a) shows the $^{19}$F MAS spectrum of PVDF powder involving the α-form. The two peaks at −79 and −93 ppm were assigned to the crystalline TG$^{+}$TG$^{-}$ sequence, and the most intense peak at −88.6 ppm was assigned to the amorphous domain. The β-form having all-trans (TTTT) conformation was also observed at −93 ppm. The fact that $\delta_F$ of peak 1 is closer to −93 ppm than −79 ppm suggests that trans-conformers are predominant in the amorphous domain. Figs.1(b) and 1(c) show the $^{19}$F MAS spectra of as-received and single-crystalline (SC) films of P(VDF/TrFE), respectively. The $\delta_F$ and $T_{1p}^{F}$ of peak 1 coincides with that of the PVDF amorphous domain, and no peak is observed at −79 ppm, while the $\delta_F$ of peak 2 (−93 ppm) with a long $T_{1p}^{F}$ agrees with the β-form of PVDF. This indicates that the VDF components in the crystalline domain of the copolymer take the all-trans conformation, and those in the amorphous domain take similar structures and mobility as in amorphous PVDF.

Fig.2 shows the VT $^{1}$H→$^{19}$F CP/MAS spectra for the CF$_2$ region of a SC-film for a short contact time (0.1 ms). At elevated temperatures, a new peak with a small linewidth (peak 1’: −86.8 ppm) appeared at higher frequency than peak 1, suggesting a larger content of gauche conformers than for amorphous PVDF. The $T_{1p}^{F}$ of each signal (>40 ms) promptly decreased above 107ºC and became identical (ca.20 ms) at 119ºC for all peaks. In addition, the all-trans crystalline signal (peak 2) disappeared between 115 and 119ºC. It has been proposed that rotational motion occurs along each polymer chain in the paraelectric phase. The changes in $T_{1p}^{F}$ and in the $^{19}$F spectral shapes indicate that the phase transition occurred between 115 and 119ºC, and that rotational motion gave statistically mixed TG$^{+}$, TG$^{-}$, T$_3$G$^{+}$, and T$_3$G$^{-}$ at the higher temperatures.

Acknowledgement: We thank D.C. Apperley and P. Wormald for the help of measurements and discussions. 