SOLID-STATE ^{19}F MAS NMR ANALYSIS OF THE γ-PHASE OF POLY (VINYLIDENE FLUORIDE)

Jin-Woo Park[a],, Il Kim[a], Keitaro Aimi[b], Shinji Ando[b], and Chang-Sik Ha[a]

[a]Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea
[b]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-Ku, Tokyo 152-8552, Japan

Introduction

Solid-state ^{19}F MAS NMR using spin-lock experiments spectroscopy shows that significant differences exist in the ^{19}F spin-lattice relaxation times in the rotating frame ($T_{1\rho}^{F}$) between the immobile (crystalline) and mobile (amorphous) regions for semi-crystalline fluoropolymers[1-4]. The value of $T_{1\rho}^{F}$ is shorter for amorphous chains than it is for crystalline regions. In addition, Holstein *et al.*[1] have shown, by partial conversion of the α-form into the β-form, that the β-form having all-*trans* conformation displays a single signal at δ_F = –98 ppm, whereas the α-form having *t*-g^+-*t*-g^- conformation displays two resonances at δ_F = –82 and –98 ppm.

One of us[3] has investigated the ^{1}H →^{19}F/^{19}F→^{1}H CP/MAS and inversion recovery CP/MAS spectra of PVDF powder. The significant differences observed for the effective time constants, $T^{\#}_{HF}$ and $T^{\#}_{1\rho}$, estimated from the ^{1}H→^{19}F CP curves, clarify that significant differences exist in the strengths of the dipolar interactions between the crystalline and amorphous domains. In addition, the inverse ^{19}F→^{1}H CP/MAS and ^{1}H→^{19}F CP/drain MAS experiments provided information complementary to that from the ^{1}H→^{19}F CP-MAS spectra. In the present study, we have conducted solid-state ^{19}F MAS NMR spectroscopic investigations to determine the crystalline structure of the γ-phase of PVDF.

Experimental

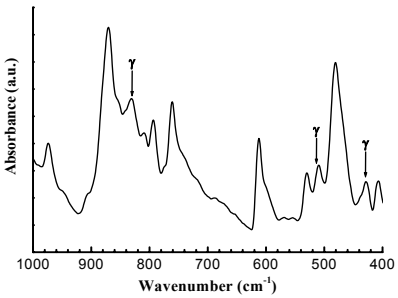
Materials The PVDF powder (M_n = 150,000; M_w = 300,000) that we have used is KF-1100, which was supplied by Kureha Chemical Industry Co., Ltd. (Japan). The intrinsic viscosity of this PVDF is 1.1 dL/g in dimethylacetamide (DMAc) at 25 °C; it has about 3% structural defects (head-to-head or tail-to-tail bonds), as determined by ^{19}F NMR spectroscopy. We prepared typical PVDF films of the γ-phase. These films were prepared by annealing spin-coated PVDF films at 170°C for 12 h, followed by cooling at a normal rate (e.g., 10–20°C/min, or higher)[5].

Instrumentation. Solid-state ^{19}F MAS NMR spectroscopic measurements were performed on a JEOL EX spectrometer. We operated the spectrometer at resonance frequencies of 282.65 and 300.40 MHz to obtain fluorine-19 and proton spectra, respectively. Samples were spun at the magic angle at rate of 16 kHz. We used a commercial (Chemagnetics) ^{1}H–^{19}F double-tuned APEX MAS probe capable of high-power heteronuclear decoupling and fitted with a 4-mm o.d. zirconia Pencil. The ^{19}F spin-lattice relaxation times in the rotating frame ($T_{1\rho}^{F}$) were measured at a spinning speed of 16 kHz using the H–F probe by means of the variable-time spin-lock technique. Chemical shifts in ^{19}F NMR spectra are quoted with respect to the signal for $CFCl_3$ and were measured via replacement with a sample of liquid C_6F_6 (-163.6 ppm) with proton decoupling. The recycle delays of 5.0 s were sufficiently long compared with the spin-lattice relaxation time in the laboratory frame of the sample (T_1^F = 0.5 s; T_1^H = 0.8 s). In this study, the magnitude of the ^{1}H decoupling was ca. 75 kHz.

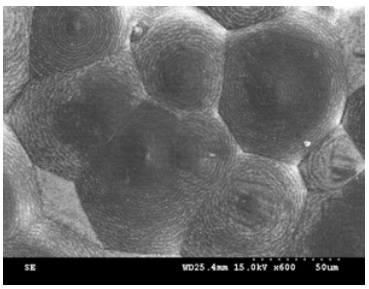
Results and Discussion

Figure 1a displays the IR spectrum of γ-form PVDF films. The bands at 835, 510, and 430 cm^{-1}, which are indicated by arrows, are all assignable to the γ-phase[6]. Moreover, a scanning electron microscopy (SEM) image (Fig. 1b) of the annealed PVDF films clearly exhibits a spherulitic γ-phase.

We attempted to characterize this γ-form film by solid-state NMR spectroscopy. Figure 2 displays the ^{19}F MAS NMR spectrum, which exhibits two new peaks at –84.2 and –101.3 ppm in addition to five peaks (α-form PVDF) at –79.6, –88.5, –93.7, –110.4, and –112.4 ppm. Table 1 summarizes the estimated $T_{1\rho}^{F}$ values obtained by fitting the spin-lock decays using single or double-exponential functions. The decays of the crystalline peaks (D and G) and new peaks (C and F) have long $T_{1\rho}^{F}$ components; the amorphous peaks (A, B, and E) have relatively short $T_{1\rho}^{F}$ components. These results indicate that the newly observed peaks for γ-phase are undoubtedly assignable to the crystalline phase.



(a)



(b)

Figure 1. (a) FTIR spectrum (the bands at 835, 510, and 430 cm^{-1} are all assignable to the γ-phase; those peaks are indicated by arrows) and (b) scanning electron microscope image of the γ-form of the PVDF film. Conditions; annealed for 12 h at 170 °C

In the $T_{1\rho}^{F}$ measurement and the ^{19}F MAS NMR spectra, the PVDF film having the γ-crystalline form exhibits seven resonances that we attribute to amorphous domains (–88.5 ppm), crystalline domains (–101.3, –93.7, –84.2, and –79.6 ppm), and regio-irregular structures (–112.4 and –110.4 ppm). The reason that γ-form displays four resonances is attributed to the *t*-*t*-*t*-g^+-*t*-*t*-*t*-g^- conformation.

Conclusions

We investigated the crystalline structures of γ-form PVDF film by FT-IR, SEM and solid-state ^{19}F MAS NMR spectroscopy. ^{19}F MAS NMR spectra obtained from spin-lock experiments are very sensitive to the crystalline structures of PVDF and, hence, the relative population and molecular mobility of each morphological component could be estimated quantitatively. ^{19}F MAS NMR spectra of γ-form PVDF film display two new distinct shoulders at lower (–101.3 ppm) and higher (–84.2 ppm) frequencies; they possess long values of $T_{1\rho}^{F}$ (typical for crystalline components) and their chemical shifts are significantly different from those of the α and β phases.

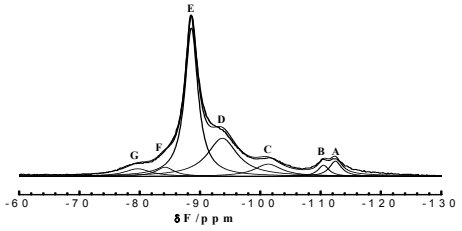
Acknowledgements. The work was partly supported by the KAIST-TIT Joint Exchange Program through the KOSEF and JSPS sponsorship. This work was partly supported by the National Research Laboratory Program, the Center for Integrated Molecular Systems, POSTECH, Korea, and the Brain Korea 21 Project for their financial support. This work was also partly supported by Grant-in-Aid for scientific research (No.13450387) from the Japan Society for the Promotion of Science (JSPS).

References

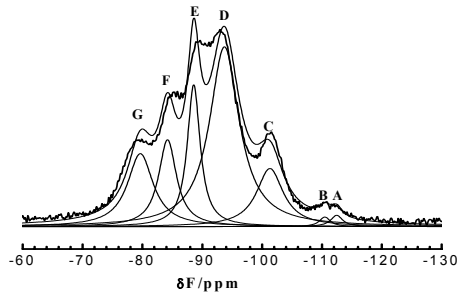
(1) Holstein, P.; Harris, R. K.; Say, B. J. *Solid State Nucl. Magn. Reson.* **1997**, *8*, 201.
(2) Ando S.; Harris, R.K.; Holstein, P.; Reinsberg S.A.; Yamauchi, K. *Polymer*, **2001**, *42*, 8137.
(3) Ando, S.; Harris, R. K.; Reinsberg, S.A. *Magn. Reson. Chem*. **2002**, *40*, 97.
(4) Ando, S.; Harris, R. K.; Scherer, U. *Suppl. Encyclop. NMR*, **2002**, *9*, 531.
(5) Hasegawa, R. *Polym. J.* **1972**, *3*, 591.
(6) Gregorio, R. Jr; Cestani M.J. *J. Polym. Sci., Part B, Polym. Phys.*, **1994**, *32*, 859.

Table 1. The spin-lattice Relaxation in the Rotating Frames of Each Spectral Component in the Solid-state ^{19}F MAS NMR Spectra of the γ-form

Chemical shift (ppm)	Symbol	Width at half-height	Relative intensity (%)	$T_{1\rho}^{F}$ (ms)
-112.4	A	1.2	4.4	1.5 (66.7%) 12.2 (33.3%)
-110.4	B	1.1	3.0	1.7 (50.6%) 8.5 (49.4%)
-101.3	C	2.7	8.2	6.1 (21.9%) 22.2 (78.1%)
-93.7	D	3	28.1	1.6 (23.6%) 18.7 (76.4%)
-88.5	E	1.7	47.4	1.8 (59.2%) 6.8 (41.8%)
-84.2	F	1.8	4.1	17.1 (100%)
-79.6	G	2.6	4.8	22.1 (100%)



(a)



(b)

Figure 2. Comparison of (a) directly polarized and (b) crystalline-selective ^{19}F MAS NMR spectra of γ-form PVDF film under a MAS rate of 16 kHz. Experimental parameters: fluorine π/2 pulse duration 2.5 μs, 32 transients, recycle delays 6s, spin-locking time for (b) 20 ms. The spectra were decomposed using seven Lorentzian functions.