SHORT COMMUNICATIONS

**Molecular Motions of Amorphous Piezoelectric Polymers
Determined by ^{13}C CPMAS NMR Spectroscopy**

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As reported previously, the microstructure of copoly(vinylidene cyanide/vinyl acetate), P(VDCN/VAc), and copoly(vinylidene cyanide/methyl methacrylate), P(VDCN/MMA), has been successfully determined by 125 MHz ^{13}C NMR spectroscopy in solution.^{1,2} The microstructure of P(VDCN/VAc) and P(VDCN/MMA) is almost identical; namely, these two copolymers are highly alternating with completely atactic structures (*i.e.*, ε -isotacticity $\sigma_\varepsilon \cong 0.5$). The former copolymer has recently received considerable attention in its high piezoelectricity even in the amorphous phase,^{3,4} whereas the latter does not show any noticeable piezoelectricity, the piezoelectric d constant of which is one order lower than that of P(VDCN/VAc).⁵

During the past several years the combination of crosspolarization (CP),⁶ high power dipolar decoupling (DD) and magic angle spinning (MAS)⁷ techniques has provided high resolution NMR spectra in solid polymers.⁸ In this communication, we investigate the molecular dynamics by using the ^{13}C CPMAS NMR spectroscopy, in order to clarify the

above difference of the piezoelectricity between P(VDCN/VAc) and P(VDCN/MMA). The CPMAS NMR method is applicable to amorphous polymers to study the molecular structure and the molecular dynamics, whereas X-ray diffraction is only for crystalline polymers. Different from the crystalline piezoelectric polymers, the piezoelectricity of amorphous polymers is mainly dependent upon the individual molecular rearrangement. The poling transforms the molecular arrangement in such a way to orient the dipole moment parallel to the film thickness direction. The molecular rotational motions along the main chains are important in determining the dipole moment orientation, and also piezoelectricity. Such rotational motions can be generally detected by proton spin-lattice relaxation time $T_{1\rho}(\text{H})$ in the rotating frame. This communication describes preliminary ^{13}C CPMAS NMR studies of P(VDCN/VAc), P(VDCN/MMA), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA). Powder samples of P(VDCN/VAc) and P(VDCN/MMA) were generous gifts from

Figure 1. 67.8 MHz ^{13}C CPMAS NMR spectra of poly(methyl methacrylate) (PMMA), copoly(vinylidene cyanide/methyl methacrylate) (P(VDCN/MMA)), poly(vinyl acetate) (PVAc) and copoly(vinylidene cyanide/vinyl acetate) (P(VDCN/VAc)). All the spectra were recorded under a decoupling field strength of 44 kHz with a CP time of 1 ms and a repetition time of 5.0 s.

Mitsubishi Petrochemical Co., Ltd. Commercial samples of PVAc and PMMA were obtained from Kuraray Co., Ltd. and Mitsubishi Rayon Co., Ltd., respectively. The spectra were obtained at 67.8 MHz on a JEOL JNM GX 270 spectrometer, using a MAS rate of about 3.8 kHz. The $T_{1\rho}(\text{H})$ was obtained from the plots of the final evolution of the carbon signal intensity vs. the contact time in a CP experiment. A matched spin-lock cross-polarization transfer employed a B_1 of 44 kHz.

^{13}C CPMAS spectra of PMMA, P(VDCN/MMA), PVAc and P(VDCN/VAc) are shown in Figure 1. The corresponding assignments of P(VDCN/VAc) and P(VDCN/MMA) have been made by comparison of spectra in solutions,^{1,2} while the assignments of PVAc and PMMA make reference to references 9 and 10, respectively. Most of resonance lines of these four samples are well-resolved except broad peaks from the cyanide carbon and the carbonyl carbon of P(VDCN/VAc) and P(VDCN/MMA) due to overlapping with spinning side bands. It should be noted that the linewidth of the methylene peak for P(VDCN/VAc) is much smaller than that for PVAc, while the corresponding linewidths for both P(VDCN/MMA) and PMMA are approximately

the same. Such line broadening may be associated with conformational effects as well as the molecular mobility. As will be explained later, the latter is a more dominant factor of this line broadening. Hence, the motional averaging of main chains is more efficient for P(VDCN/VAc) compared with that for PVAc; namely, P(VDCN/VAc) is more mobile than PVAc.

The $T_{1\rho}(\text{H})$ is effectively used to study the low-frequency motions, *e.g.*, local molecular motions including molecular rearrangement. These $T_{1\rho}(\text{H})$ values at B_1 of 44 kHz for PVAc, P(VDCN/VAc), PMMA and P(VDCN/MMA) are compiled in Table I. From the uniformity of $T_{1\rho}(\text{H})$ for a given sample regardless of the species of carbon resonance lines through the spin-diffusion relaxation mechanism, it is clarified that all these four amorphous samples are homogeneous in structure without any local structures or microdomains. This can be also understood by measuring the temperature dependence of the dynamic mechanical modulus.¹¹ As seen in Table I, the $T_{1\rho}(\text{H})$ value of PVAc is larger than that of P(VDCN/VAc), while the opposite situation is found in the comparison between PMMA and P(VDCN/MMA).

In discussing $T_{1\rho}(\text{H})$ data, we have to know

Table I. Proton $T_{1\rho}$ from proton-carbon cross-polarization at H_1 of 44 kHz for poly(vinyl acetate), copoly(vinylidene cyanide/vinyl acetate), poly(methyl methacrylate), and copoly(vinylidene cyanide/methyl methacrylate)

Carbon species ^b	PVAc	P(VDCN/VAc)	PMMA $T_{1\rho}(\text{H})/\text{ms}$	P(VDCN/MMA)
CH_3	21.13 (± 2.2)	17.23 (± 3.2)		
CH_2	20.99 (± 0.12)	17.07 (± 0.09)	15.3 (± 0.1) ^a	18.25 (± 0.62) ^a
αCH_3			9.83 (± 0.02)	19.5 (± 0.1)
CH	22.52 (± 0.39)	18.32 (± 0.02)		
OCH_3			15.0 (± 0.1) ^a	22.1 (± 0.05) ^a
$-\text{C}-$ (MMA)			11.50 (± 0.18)	15.14 (± 0.01) ^a
$-\text{C}-$ (VDCN)		20.43 (± 0.31)		20.49 (± 0.25)

^a Data estimated from height intensities.

^b See Figure 1.

whether correlation time is larger or smaller than the reciprocal of the spin-lock field intensity ω_1 of proton. The crude dependence of $T_{1\rho}(\text{H})$'s on correlation time is quite the opposite, depending on whether it is larger or smaller than ω_1^{-1} . Glass transition temperatures are very effective in this judgment. DSC measurements were done by a DC 10 manufactured by Seiko Electronics Industry, Inc. The glass transition temperatures of PVAc, P(VDCN/VAc), PMMA and P(VDCN/MMA) were 28°C, 160°C, 105°C, and 147°C, respectively, from DSC curves, so that the correlation time at room temperature is apparently larger than ω_1^{-1} for all four samples. This leads to an important conclusion that the local molecular motion of P(VDCN/VAc) is more rapid than that of the PVAc homopolymer while the corresponding motion of P(VDCN/MMA) is slower than that of the PMMA homopolymer. As mentioned earlier, the line shapes of methylene carbon peaks in Figure 1 support the above conclusion. According to the Corey–Pauling–Koltun (CPK) space filling molecular model of P(VDCN/MMA), moreover, molecular rotational motion along the main chain is considerably restricted by steric hindrance between the cyanide group in the VDCN unit and the $\alpha\text{-CH}_3$ group in the MMA unit. Therefore, we can understand why the piezoelectric activities between P(VDCN/VAc) and P(VDCN/MMA) are different in spite of their same microstructures. During the poling process, molecular rotation occurs more efficiently for P(VDCN/VAc) compared with that for PVAc, whereas in the case of P(VDCN/MMA) such a

rotational motion hardly occurs under the d.c. electrical field (300 kV cm^{-1}) due to large steric hindrance. Hence, this rigid structure of P(VDCN/MMA) results in low piezoelectricity. The ^{13}C CPMAS NMR spectra successfully explain the piezoelectric origin for P(VDCN/VAc) and P(VDCN/MMA) copolymers by introducing $T_{1\rho}(\text{H})$ data.

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