The Local Structure around Sodium Ions in Poly(ethylene-ran-methacrylic acid) Ionomers Studied by ^{23}Na Solid-state NMR under a High Magnetic Field, 21.9 T

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The local structure of sodium ions in poly(ethylene-ran-methacrylic acid) ionomer neutralized by sodium hydroxide has been investigated using ^{23}Na MAS and multiple-quantum-magic-angle-spinning (MQMAS) NMR techniques at a high magnetic field. Isotropic chemical shifts and quadrupolar coupling products of three kinds of nonequivalent ^{23}Na ions, i.e., isolated, hydrated, and aggregated ^{23}Na ions were estimated from peak positions in ^{23}Na MQMAS spectra. The MQMAS technique at high magnetic fields is expected to be a powerful tool to investigate the local structure in amorphous systems containing quadrupole nuclei.

Ethylene ionomers are copolymers consisting of ethylene nonpolar backbones and acid groups, such as carboxyl, sulfonic, and pyridium groups, up to 10%. It is well known that partial or full neutralization of ionic groups in the polymer causes internal aggregation. The resulting cross-linking structure is believed to improve tensile strength, impact resistance, and thermal properties of the polymer. Many researches have been reported on the microstructure of ionomers using small-angle X-ray scattering, differential scanning calorimetry, infrared spectroscopy, dynamic mechanical spectroscopy, dielectric relaxation measurements, and electron spin resonance to understand improving mechanisms.[1] The solid-state NMR spectroscopy is one of powerful tools to investigate local structures and dynamics in solid amorphous systems. Many NMR studies on polymer matrices, crystallinity, ionic groups, and metal cations have been reported.[2,3] Most metal cations consist of half-integer quadrupole nuclei showing the quadrupole effect; especially, the second-order quadrupole coupling (SOQC) gives complicated NMR spectra. Multiple-quantum-magic-angle-spinning (MQMAS) technique was recently developed by Frydman and co-workers for acquiring high-resolution spectra of half-integer quadrupole nuclei.[4] Further detailed structural information around half-integer nuclei is obtainable from the two-dimensional NMR technique of MQMAS. It is noted that SOQC effects can appreciably be reduced and high resolved spectra are obtainable by applying high-magnetic fields.[5] In this report, the local structure around ^{23}Na ions in the ethylene ionomer was investigated by measuring ^{23}Na MAS and MQMAS NMR spectra at high-magnetic field of 21.9 T.

Poly(ethylene-ran-methacrylic acid) containing 3.5 mol % methacrylic acid (E-MAA) was kindly supplied by Mitsui-Dupont Chemical Co., Ltd. E-MAA was gradually neutralized by immersing into sodium hydroxide–methanol for one week at 50 °C. The obtained sample, (E-MAA-Na), was dried under vacuum at room temperature for one day and then stored at room temperature. The degree of neutralization estimated by IR spectroscopy was about 90%. The ^{23}Na MAS and MQMAS NMR spectra were recorded on JEOL ECA 930 and 500 spectrometers equipped with a JEOL 4 mm MAS probe and a Varian Chemagnetics T3 4 mm MAS probe, respectively. The ^{23}Na resonant frequency was 249.0 MHz at 21.9 T and 132.3 MHz at 11.8 T. The MAS frequency of 15 kHz was stabilized within ±10 Hz by a JEOL MAS speed controller. The ^{23}Na chemical shift was referenced to NaCl crystalline powder as an external reference at 7.1 ppm. A three pulse sequence employing z-filter[6] was used for acquiring the triple-quantum (3Q) MAS NMR spectrum. All spectra were collected at room temperature. A pulse delay of 6 s after the acquisition of free induction decay was enough to obtain fully relaxed ^{23}Na spectra.

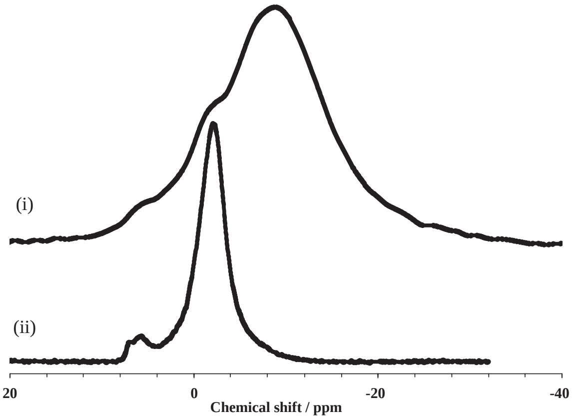

Figure 1. ^{23}Na MAS NMR spectra of E-MAA-Na at room temperature at magnetic fileds, 11.8 (i) and 21.9 T (ii).

Figure 1 shows the ^{23}Na MAS NMR spectra of E-MAA-Na at 11.8 (i) and 21.9 T (ii) at room temperature. A broad peak spread over from 12 to −26 ppm was observed at 11.8 T as shown in (i), while, at 21.9 T, two peaks, one strong peak observed around −2 ppm and the other peak around 7 ppm can be seen in (ii). The broad peak observed at 11.8 T seems to consist of multipeaks, and this peak is appreciably distinguished as two peaks in the measurement at the high field. The shoulder obtained in the low-field side (i) seems to correspond to the peak at 7 ppm in (ii). The other peaks are expected to be shifted to the low field, because of the SOQC reduction at the high magnetic filed, and these peaks probably correspond to the strong peak in (ii). These peaks reflect either the CS distribution or the second-order quadrupolar line shape.

Figure 2 shows an ^{23}Na MQMAS NMR spectrum of E-MAA-Na at room temperature observed at 21.9 T. CS and QIS represent the chemical shift and quadrupole-induced shift axes, respectively. The projection of the isotropic spectrum onto the

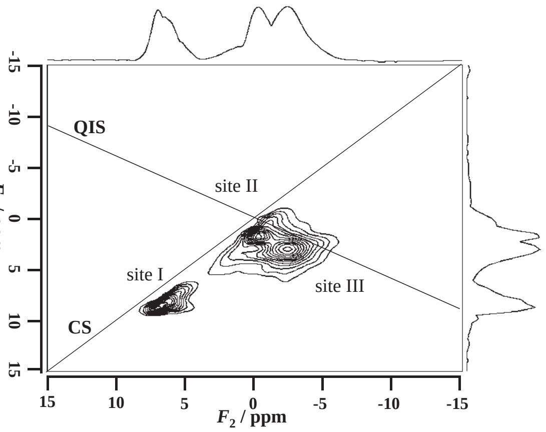

Figure 2. An ^{23}Na MQMAS NMR spectrum and projections to F_1 (isotropic spectrum) and F_2 (MAS spectrum) dimensions of E-MAA-Na at room temperature under, 21.9 T. CS and QIS represent the chemical shift and quadrupole-induced shift axes, respectively.

F_1 axis relates to the ^{23}Na high-resolution spectrum excluding the quadrupole effect, while that onto the F_2 axis to the ^{23}Na MAS NMR spectrum. The asymmetric structure for the peaks in the F_2 projected spectrum is caused by the SOQC, which should be symmetric in the F_1 projected spectrum. Clearly three peaks appear in the MAS spectrum projected on F_2 axis. In usual 1-D MAS spectrum measurements, it is often observed that peaks of minor components are covered over by those of major components. We could show the presence of three kinds of Na^+ sites in the present system in MQMAS spectra. The peaks, named Site I, II, and III in 2-D dimension are expected to be assigned to isolated ion pairs, hydrated ions and aggregated ions, respectively, according to the ^{23}Na NMR study in sulfonated polystyrene ionomers by Cooper et al.[3]

The isotropic chemical shift ($\delta^{cs}{}_{iso}$) and the quadrupole coupling products given by $P_q = C_q(1 + \eta^2/3)^{1/2}$, where $C_q = e^2qQ/h$ and η is the quadrupolar asymmetry parameter, can be estimated from peak positions δ_{MAS} and δ_{iso} in the MQMAS spectrum.[7] The δ_{MAS} observed is the sum of two isotropic components, $\delta_q{}^{(2)}$ and $\delta^{cs}{}_{iso}$. $\delta_q{}^{(2)}$, the second-order isotropic chemical shift is always negative and depends on the magnetic field. The $\delta^{cs}{}_{iso}$ and P_q values at Site I, II, and III are shown in Table 1. These values are evaluated by taking averaged positions. Sites I and II locate close to the chemical shift (CS) axis comparing to Site III, implying small SOQC values ($\delta_q{}^{(2)}$). Site I is supposed to consist of two components, since the F_1 projected spectrum shows an anisotropic shape. One is mainly elongated along the CS axis, implying an amorphous structure, the other is along F_2 axis. The peak is elongated along the CS axis, meaning an amorphous structure. Those results obtained might indicate the presence of the isolated ions in two different environments. Site II also seems to consists of two components, the broad and narrow peaks. Particularly, the narrower one implies a small P_q attributable to $^{23}Na^+$ ions interacting with water molecules as shown in Table 1. The P_q value depends on the tensor of the electric field gradient made by atomic groups surrounding $^{23}Na^+$ ions. Site III with a comparably large P_q is relatively broadened along the F_2 axis rather than the CS axis. In Site III, it is expected that $^{23}Na^+$ ions make bi- or tetra-coordinated associations with carboxyl groups.[1]

Table 1. Isotropic, MAS, chemical shifts (δ_{iso}, δ_{MAS}, $\delta^{cs}{}_{iso}$),[a] and quadrupolar coupling products (P_q) for Site I, II, and III, respectively, at room temperature

	δ_{iso}/ppm/ ± 0.1	δ_{MAS}/ppm/ ± 0.1	$\delta^{cs}{}_{iso}$/ppm/ ± 0.1	P_q/MHz/ ± 0.1
Site I	8.6	7.0	8.0	1.7
Site I	7.9	6.2	7.3	1.8
Site II	1.7	−0.3	1.0	1.9
Site III	2.9	−2.4	0.9	3.1

[a] Detailed explanations for δ_{iso}, δ_{MAS}, and $\delta^{cs}{}_{iso}$ refer to ref 7.

In summary, the local structure of $^{23}Na^+$ ions in E-MAA-Na was investigated by the ^{23}Na MQMAS technique at high magnetic fields. The products of respective isotropic chemical shifts and quadrupolar coupling constants of isolated ion pairs, hydrated ions, and aggregated ions were estimated. It could be derived from the MQMAS spectrum that the isolated and hydrated ions are located at two different environments, respectively. This result will be confirmed by using samples annealed at various temperatures and also by applying the HETCOR technique between ^{23}Na and ^{13}C nuclei. Here, we can conclude that the MQMAS technique at a high magnetic field is a powerful tool for investigating the local structure even in amorphous state, although nuclei with relatively large quadrupole coupling constants give complicate NMR spectra.

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