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^{23}Na-NMR of solid state ionomers: lineshape, shift, and hydration effects

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SUMMARY

^{23}Na-NMR spectra at 52.9 MHz have been obtained for a series of sodium sulfonate and carboxylate model compounds and for solid poly(styrene-co-styrene sulfonate) and poly(ethylene-co-methacrylic acid). Spectra of the model compounds show spin-rate independent features resembling pure quadrupolar lineshapes, but with anomalies. ^{23}Na-NMR spectra of the dried ionomers are featureless and much broader than those of the models and are shifted 30-40 ppm upfield from NaCl. The sulfonated ionomer spectrum changes to a narrow line at 0 ppm upon exposure to 45% humidity at 20°C for 12 hours. The carboxylic ionomer shows no change on room temperature air exposure but 12 hours at 95°C in water-saturated air changes the spectrum markedly with some evidence for exchange among water and carboxyl groups. This type of experiment with a range of acid and Na content under rigidly controlled conditions should help elucidate the aggregation of salt groups in various ionomers.

INTRODUCTION

One of the intriguing structural questions in polymer science is the arrangement of salt groups in ionomers. Some sort of salt group aggregation is generally held responsible for property enhancement such as toughness, melt viscosity, modulus, etc., commonly observed in these materials. Ionomers, such as Surlyn,^{R} contain a few percent acidic co-monomers such as methacrylic acid in addition to polyethylene. Usually the acid groups are at least partially neutralized with metal hydroxides yielding a Na or Zn content of a few weight percent. There is a great deal of physical data on such systems (1) and a number of theories regarding details of structure of ionic groups. These theories are supported mainly by x-ray diffraction and scattering data. A Mössbauer spectroscopy study (2) on Fe^{+2} salts gave evidence for dimers, clusters, and quasi isolated complexes in vinyl-pyridine/polybutadiene ionomers. This probably represents the best spectroscopic study of the arrangement of ions in ionomers but quite obviously Fe^{+2} is not of general interest, and may not be structurally representative. Many studies of the hydration and coordination of the ionic moieties in ionomers have been done in solution (3,4). Recent advances

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in Nuclear Magnetic Resonance (NMR) have brought forth the possibility of observing reasonably narrow resonances in the solid state. Solid state ^{23}Na-NMR has been pioneered by Oldfield and Kirkpatrick (5) for various minerals and simple compounds, overcoming the initial impression that quadrupolar interactions ($I = 3/2$ for ^{23}Na) would preclude observability and that small chemical shifts and broad lines (based on expectations from solution work) would make ^{23}Na studies not worth the effort. Based on Oldfield's work we were encouraged to pursue ^{23}Na-NMR spectroscopy in solid ionomers which might lead to a better understanding of the arrangement of the salt groups.

Because ^{23}Na has an electric quadrupolar moment, the lineshapes and shifts in NMR are expected to be sensitive to the charge environment around the ^{23}Na nucleus. It is to be appreciated that the combined effects of chemical shift and quadrupolar interaction tensors with the further complication of magic angle spinning will not give a lineshape readily interpretable in terms of molecular parameters such as charges and distance of ligands. However it is reasonable to expect that a variety of lineshapes may be observed which can empirically be associated with a variety of nuclear environments. The problems of NMR lineshapes for quadrupolar nuclei have been addressed for the slow spinning regime (6) and for the non-spinning regime (7) but neither study applies to our system. It is well understood that the $-1/2 \leftrightarrow +1/2$ transition will be relatively narrow for most quadrupolar cases and there will be dipolar, chemical shift, and second order quadrupolar effects present in the lineshape (5).

In this preliminary report we have investigated the ^{23}Na-NMR spectra of some simple polycrystalline "model" compounds, some NaOH neutralized 5/95 poly(styrene sulfonate-co-styrene) and 9/91 poly(methacrylic acid-co-polyethylene) [Surlyn^{R}]. We show that spectra can be fairly readily obtained, the lineshapes are reproducible and independent of spinning frequency, and, in the case of ionomers, dramatic changes occur in position and lineshape with hydration.

EXPERIMENTAL

Spectra were obtained at 52.9 MHz on an IBM 200 AF spectrometer with a multinuclear probe manufactured by Doty Scientific (Columbia, S.C.). Spinning at about 4500 Hz was at the magic angle. Most spectra were obtained with high power decoupling during accumulation after a 3.3 μs pulse. The pulse length was set for maximum ^{23}Na signal intensity, and solid NaCl was used as a chemical reference with $\sigma = 0$. Recycle time was 1 second. The probe was tuned with a special insert capacitor to minimize reflected power at 52.9 MHz but the ^{13}C-preamp was used *in lieu* of a broad banded or selectively tuned preamp and gave a quite strong signal. The signal-to-noise under roughly comparable conditions was about 20 times that for ^{13}C observation by direct polarization.

Surlyn samples were used as received. The poly(styrene sulfonate-co styrene) was dissolved in 1,2-dichloroethane titrated with methanolic NaOH and precipitated in isopropanol.

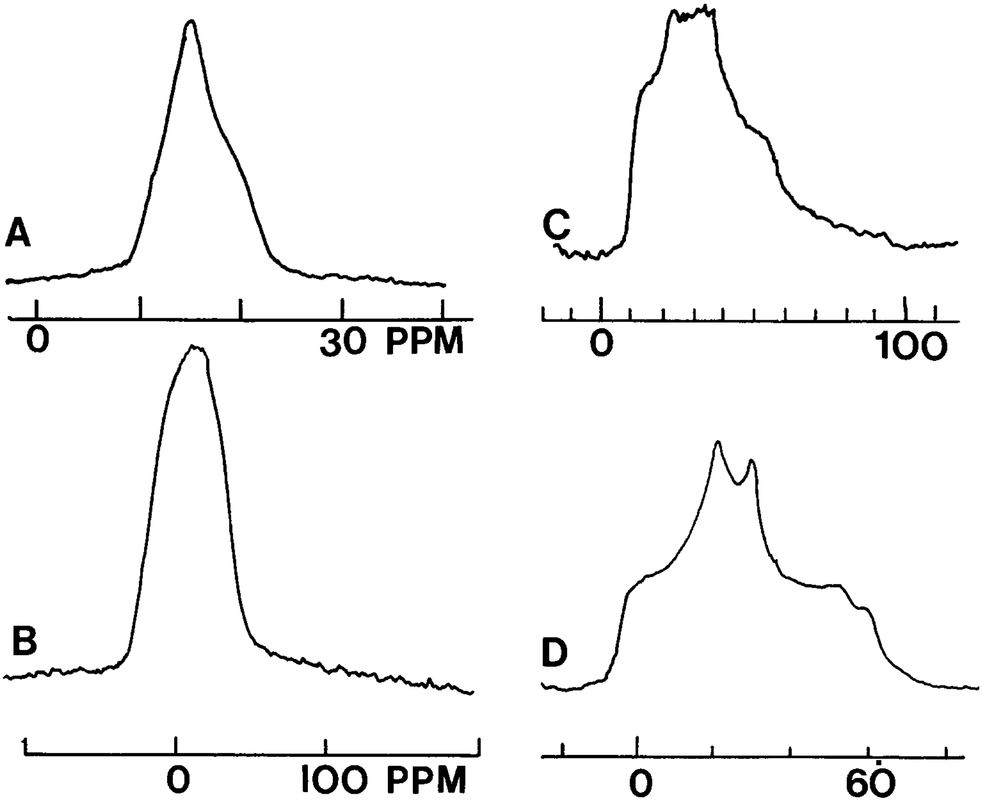


Figure 1. ^{23}Na-NMR Spectra of a series of 'model' sulfonate and carboxylate coordinating compounds at 52.93 MHz. All spectra were obtained with a 3.3 μs pulse, 1 second recycle time and are referred to NaCl as $\sigma = 0$. Full decoupling power of protons was applied during acquisition. Line broadening (LB) of exponential multiplier before Fourier transforming and number of scans (NS) vary as indicated. Spinning was at 4500 rps except for Figure 1B.

(A) Sodium-p-toluene sulfonate NS = 41, LB = 20.
(B) Sodium-p-toluene sulfonate NS = 1400, LB = 50 (non-spinning).
(C) Sodium benzoate NS = 1400, LB = 50.
(D) Disodium ethylene diamine tetraacetic acid NS = 465, LB = 100.

RESULTS

Model Compounds

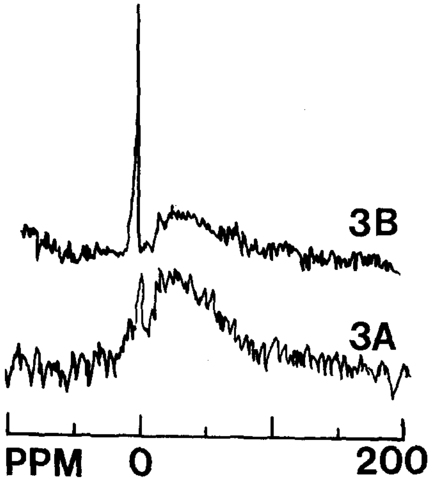
In Figure 1 are shown the ^{23}Na NMR spectra of sodium paratoluene sulfonate (NaPTS) MAS (A), NaPTS, non-spinning (B), sodium benzoate (C), disodium ethylenediamine tetraacetic acid (D). In all these cases as the spinning rate is lowered sidebands move in toward the centerband which decreases correspondingly in intensity but there is no change in the basic lineshape of the central transition. Cessation of spinning causes a marked broadening and loss of features as in the comparison of Spectra 1A and 1B where a five-fold increase in width of the lineshape is seen. Without spinning the ^{23}Na-NMR spectrum of EDTA becomes 150 ppm broad at the base and all features are lost. Similarly without decoupling the EDTA lineshape loses all sharp features and is broadened.

Spectrum 1C and 1D are strongly similar to the generalized quadrupolar lineshape (Figure 7 of reference 7) for anisotropy parameter ($\eta = (q_{xx} - q_{yy})/q_{zz}$ where q_{ii} is the potential gradient in the i direction at the nucleus), $\eta > 1/3$. These lineshapes show the high and low field edges, as well as the two singularities which may correspond with $-16(1 - \eta)$ and $8(1 - \eta^2)$ in pure second order broadened quadrupolar $1/2 \leftrightarrow -1/2$ transitions. Using the four analytical expressions for the two edges and two singularities one can calculate "e^2Qq" and "η" values from our observed lineshapes. With more equations than unknowns, the consistency check proves useful. In the case of sodium benzoate (1C) the results are reasonably self consistent with $\eta = 0.75$, $e^2Qq = 0.372$ MHz considering the error in the position of the singularities, the zero point, and the edges. In the case of Na_2EDTA (10) the consistency is poor with $\eta = 0.8$ and e^2Qq ranging from 0.4 to 0.6 depending on which edge is used. In other words the shape does not consistently fit the criterion for the pure second order broadened quadrupolar case. Detailed explanation must await further analysis but the contributions of averaged chemical shift probably complicates the shape as there is a fairly large upfield shift of the line center.

Ionomers

Figure 2 shows the ^{23}Na-MAS-NMR spectrum of Surlyn, 9% MAA by weight and 23% neutralized. The lineshape is featureless, appears to be broader than Lorentzian and at the base is about twice as wide as the lineshape of the simple compounds of Figure 1. A second sample of the same polymer 54% neutralized gave a spectrum indistinguishable from that of Figure 2 but of relative intensity 2.6. Prolonged exposure to 45% humidity air caused no change in the signal, however at elevated temperatures (Fig. 2B) a narrower signal appeared at -12 ppm while part of the broad signal remained. The shift observed in ^{23}Na-NMR of Surlyns is probably related to that in Nafion solutions. In that case (3) exchange averages these two types of signals. The residual breadth and shift of the -12 ppm peak suggests incomplete averaging or solvation in the Surlyn case.

Figure 3A shows the ^{23}Na MAS-NMR spectrum of 100%



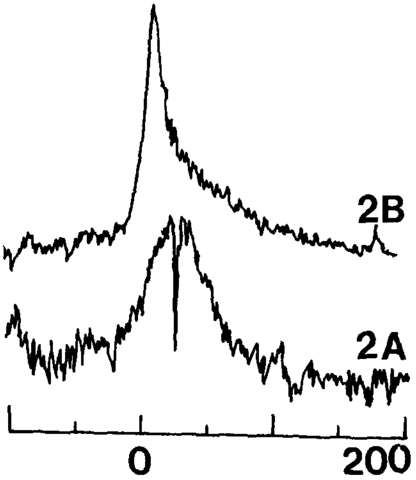


Figure 2. ^{23}Na-MAS NMR Spectrum of 9/91 poly(methylacrylic acid-co-ethylene). (A) 23% neutralized with NaOH NS = 48456, LB = 50. (B) 54% NaOH neutralized exposed to saturated water vapor at 93°C for 24 hours, NS = 22900, LB = 50.

Figure 3. ^{23}Na-MAS NMR Spectra of 100% NaOH neutralized 5/95 poly(styrene sulfonate/styrene) with conditions of Figure 1. (A) dried 2 days *in vacuo* at 120°C NS = 23178, LB = 50; (B) exposed to 45% humidity air, 22°C for 12 hours NS = 13637, LB = 50.

neutralized poly(styrene sulfonate-co-styrene). The linebreadth at base and position are comparable to those for the Surlyns but any subtleties are lost due to noise, sidebands and phasing. Exposure of sample 3A to air of 45% humidity for 12 hours yields a marked (46%) lowering of the intensity of the broad lineshape centered at -40 ppm and the appearance of a narrow signal at 0 ppm. This narrow signal is most probably due to hydration of the sodium ions with subsequent rapid motion of coordinated ligands in a way that lowers the electric field gradient on the NMR time scale.

A sample of the same copolymer which was 250% neutralized gave a spectrum very similar to that of Figure 3B even though it had been dried under conditions identical to the sample in Figure 3A. The observation of the narrow line indicates that either the excess Na^+ is in an environment which gives a narrow signal (as is the case for NaCl) or that the excess Na^+ is very difficult to dehydrate perhaps because alternative ligands (such as SO_3^- or COO^- in the case of coordinated ionomers) are not available to the hydration sphere.

The similarity of ^{23}Na-NMR signals from the two types of ionomers does suggest that the environments of the ions are similar in the two cases. The difference in susceptibility of the two species to hydration suggests significant structural differences perhaps pertaining to the integrity of permeability of the matrix around the ionic groups.

These results show the potential of ^{23}Na-NMR for exploration of ion clustering and ligand dynamics in ionomers. The contrast between the features for the model compounds and broad, shifted lineshape for the ionomers is intriguing. We are currently pursuing a project to improve signal-to-noise by using extruded samples for higher filling factors and a tuned preamplifier. The effect of variable temperature, change in signal with substoichiometric sodium levels and careful titration of the sample with water (8) are underway.

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