Pulsed NMR Study on the Hydration of Poly(acrylic acid) salts

Kyoko Hiraoka and Tetsuo Yokoyama

Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, Nagasaki, 852, Japan

Summary

Pulsed NMR was applied to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times of the equilibrium water absorbed in poly(acrylic acid) lithium salt, sodium salt, and potassium salt. T_1 and T_2 relaxation time curves for the samples of lithium and sodium salts studied showed single phase behavior, but the sample of potassium salt exhibited two-phase behavior, indicating the existence of water fraction of higher mobility.

Introduction

The preceding papers in this series (HIRAOKA and YOKOYAMA 1980 a, b, and c) have shown the drying process and equilibrium water uptake of poly(acrylic acid) sodium salts (PANa), potassium salts (PAK), and lithium salts (PALi). From the results it was considered that the vacant sites of coordination of metal atoms play an important role in the hydration behavior of poly(acrylic acid) (PAA) salts.
The object of this work is to study both the amount and strength of water binding by PAA salts. The spin-lattice and spin-spin relaxation times of the water absorbed were determined by pulsed NMR and related to the quantity of bound water and its mobility. The method for the determination has been well established and applied widely (e.g. LEUNG et al. 1976).

Experimental

Preparation of PAA salts were described in the preceding paper (HIRAOKA and YOKOYAMA 1980 a). Completely neutralized PAA salts with equilibrium water content at 25°C and 73 % relative humiduty were used for pulsed NMR measurements. Equilibrium water contents were 4.38 for PALi, 4.24 for PANa, and 5.69 for PAK(water mol/polymer repeat unit mol), respectively.

A pulsed NMR Spectrometer (10 MHz, model PR-103, The Praxis Corp., San Antonio, Texas) was used to measure spin-lattice (T_1) and spin-spin (T_2) relaxation times. For T_1 measurement, a repeated 90°, t, 90° pulse sequence was applied. For T_2 measurement, the spin-echo technique was employed. A repeated 90°, t, 180° pulse sequence was used. All the measurements were carried out at room temperature (28 ± 1 °C). Since the samples were very tacky, the bottom of the sample tube (10 mm x 75 mm) was opened and samples were introduced from the bottom by pushing with a rubber stopper. In this measurement are detected the protons of water molecules sorbed in PAA salts. The relaxation times of the protons in polymer molecules are too short to be measured.

Results and Discussion

Spin-lattice relaxation

Data for determining the spin lattice relaxation times (T_1) for PAA salts are shown in Fig. 1. The T_1 relaxation plots for PALi and PANa were linear, indicating single phase behavior. In contrast, the T_1 relaxation plot of PAK was not linear, showing multiple phase behavior. The non-exponential T_1 relaxation curve of PAK can be resolved into two exponential decay curves with relaxation times T_{11} and T_{22}, which are shown in Fig. 1. T_1 relaxation times obtained from the slopes of the straight lines ($-1/T_1$) were as follows. PALi T_1 = 19 msec, PANa T_1 = 21 msec, and PAK T_{11} = 16 msec and T_{12} = 170 msec. Thus it appears there exist species of protons with different molecular mobilities and corresponding different nuclear magnetic relaxation times in the PAK sample with equilibrium water uptake. However, single specy of protons exists in the PALi and PANa sapmples. Since a high T_1 is related to high water mobility, it is suggested that PAK is a weak water binder as compared with PALi and PANa, and that some water molecules absorbed in PAK are not bound so tightly as in PALi and PANa. The relative population of the two water species in PAK sample was estimated on the basis that the NMR signal at t = 0 is proportional to the number of protons of each specy. On this basis, the more strongly bound fraction accounted for 22.3 % of the total water. (Whether the individual relaxation times of the species can be experimentally detected depends on the exchange rates between the species. Therefore, although only single phase behavior was observed for PALi and PANa, it is possible that more than one phase was present but was not detected. However, T_2 relaxation study also suggests the existence of the single phase for PALi and PANa as described below.)
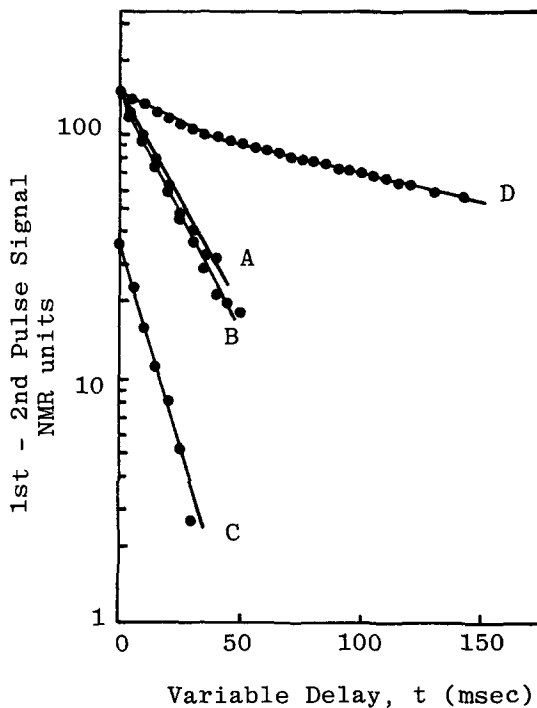
Fig. 1: Spin-lattice relaxation time (T_1)
plots for water in PAA salts.
A: PALi T_1 , B: PANa T_1 ,
C: PAK T_{11}, D: PAK T_{12}.

Spin-spin relaxation data

Fig. 2 shows the relaxation plots for PAA salts.
Single exponential decay was observed again for PALi
and PANa. However, PAK exhibited again multiple phase
behavior. The non-exponential T_2 relaxation curves
can be resolved into two exponential decay curves with
relaxation times T_{21} and T_{22}, which are shown in Fig.
2. T_2 relaxation times obtained from the slopes of
the straight lines were as follows. PALi T_2 = 6.5
msec, PANa T_2 = 8.4 msec, and PAK T_{21} = 1.3 msec and
T_{22} = 49.5 msec. The results confirms that though
only single phase of water was present in PALi and
PANa, there exist the species of protons with different
molecular mobilities in the PAK sample. The relative
population of the two water species in PAK sample was

estimated in the similar manner as T_1 relaxation study.
The more strongly bound fraction was 23.7 % of the
total water.
      The two values of the amount of water in the bound
fraction of PAK sample are in fairly good agreement if
we consider the possible errors included in the resolv-
ing process of non-exponential decay plots. The weak
water binding of PAK in comparison with PALi and PANa
may result from the smaller charge density of potassium
ion. On the other hand, water sorption studies have
shown that PAK is more hygroscopic than PALi and PANa
on the basis of water mol per repeat unit mol (HIRAOKA
and YOKOYAMA 1980 a, b, and c). This may be due to the
body-centered cubic coordination structure in PAK,
which provides more sites for hydration as described
before (HIRAOKA and YOKOYAMA 1980 b).
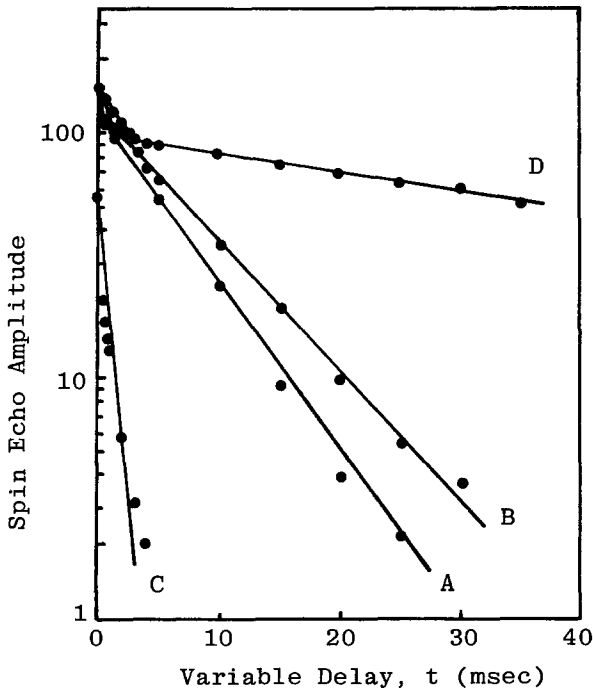   Water is a very effective plasticizer for PAA

Fig. 2: Spin-spin relaxation time (T_2) plots
        for water in PAA salts.
        A: PALi T_2 , B: PANa T_2, C: PAK T_{21},
        D: PAK T_{22}.

salts. However, for highly neutralized PAA salts containing small amounts of water, glass transitions become too vague and the estimated values of Tg sometimes seem to be unexpectedly high for its water contents. On the other hand, unfrozen water appears in sufficiently concentrated aqueous solutions of PAA salts (HIRAOKA and YOKOYAMA unpublished data). These phenomena suggest that the mobility of water molecules sorbed in ionic sites may be important to understand in detail the properties of ionic polymers. The present work is in line with this idea.

Acknowledgment

References

LEUNG, K. H., STEINBERG, M. P., WEI, L. S., and NEISON, A. I. : J. Food. Sci., 41, 297 (1976).
HIRAOKA, K. and YOKOYAMA, T. : Polym. Bull., 2, 183 (1980 a).
HIRAOKA, K., GOTANDA, M., and YOKOYAMA, T. : Polym. Bull., 2, 631 (1980 b).
HIRAOKA, K. and YOKOYAMA, T. : Polym. Bull., 3, 225 (1980 c).