

tion product between them. However, it may be said that this catalyst system is very different from the usual Kaminsky-Sinn catalysts composed of MAO and Cp_2TiCl_2 etc., which effectively catalyze olefin polymerization.

As is well-known, heterogeneous catalyst systems usually give polymers having molecular mass distributions with a broad polydispersity.⁹ However, the polydispersity of syndiotactic polystyrene obtained with the present heterogeneous catalysts was very narrow, indicating that these catalysts contain not multiple but single, equivalent active species.

In conclusion, we have prepared a new supported Kaminsky-Sinn catalyst useful for the syndiotactic polymerization of styrene.

A more detailed study is now being carried out, mainly to clarify the nature of active species in the present catalyst system, and the precise results will be published in another paper.

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Intramolecular O-H Bond Length and Quadrupole Coupling Constants of Water in Polyelectrolyte Solutions. A Nuclear Magnetic Relaxation Study

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ABSTRACT: The relaxation rates of D and ^{17}O and the rate of H due to dipolar coupling to ^{17}O were obtained in a series of poly(acrylic acid) solutions completely neutralized with lithium and cesium hydroxide. From these data the intramolecular O-H bond distance and quadrupole coupling constants have been derived. It is found that the changes in O-H bond distance and quadrupolar coupling constants induced by the charged polymer and its counterions are moderate.

Introduction

A D and ^{17}O quadrupolar relaxation study on water dynamics in linear polyelectrolyte solutions was reported recently.¹ It was found that the solvent dynamical perturbation is confined to the vicinity of the macromolecular surface. The water reorientational mobility near the chain decreases and is sensitive to the specific short-range polyion-counterion interaction. In a small-angle neutron-scattering and X-ray scattering study, a monomolecular hydration layer between the poly(methacrylic acid) (PMA) polyion and the accumulated counterions was observed.² The structure around lithium counterions in completely neutralized poly(acrylic acid) (PAA) solutions has been investigated by the first-order-difference neutron diffraction method.³ It was shown that counterions remain hydrated when they accumulate about a highly charged linear macromolecule. From these high-resolution neutron diffraction experiments it was concluded that these hydration water molecules are still oriented with their oxygen atoms toward the small ions.

The D and ^{17}O relaxation rates are completely intramolecularly determined by the quadrupolar relaxation mechanism. The corresponding correlation times refer to reorientation of the intramolecular coupling tensor; the coupling constants may depend on intermolecular interactions.

In the previous investigation on water dynamics in completely neutralized PAA and poly(styrenesulfonic acid) (PSS) solutions, a possible deviation of the coupling constants from the pure water values was not considered. However, if water molecules are hydrogen bonded to polymeric charged sites, the coupling constants may be affected considerably. Therefore, to investigate a possible change in coupling constants, the ^{17}O -induced H relaxation in ^{17}O -enriched solutions is explored and compared to D relaxation.

From this comparison, values of the intramolecular O-H bond distance and D coupling constant can be derived.⁴ The O-H bond distance provides an indication about specific interaction of a water molecule with a charged site. For instance, stretching of the O-H bond distance is observed when a water molecule coordinates to an ion such as F^- , Li^+ , Mg^{2+} , Zn^{2+} , and Al^{3+} .^{4,5} In water-dimethyl sulfoxide (DMSO) mixtures, a variation of the D coupling constant over the water fraction has been observed too.⁶ This has been attributed to specific water-DMSO interaction and/or disruption of the H bond network.

Theory

In PAA solutions the water reorientational motion occurs on the picosecond time scale.¹ As a consequence, the

Table I
Isotope Viscosity Effects Corrected Relaxation Rates and Isotopic Composition of the Samples^a

solute	C_p , monomol/kg	n	P_{17}	P_{18}	R_H , s ⁻¹	R_O , s ⁻¹	R_D , s ⁻¹
LiPAA	0.935	0.0078	0.0020	0.0015	0.508	246	3.20
	0.937						
	0.930						
	0.937						
	0.938						
	0.939						
CsPAA	0.967	0.0044	0.0052	0.0040	0.467	194	2.66
	0.972						
	0.939						
	0.972						
	0.974						
	0.978						

^a An isotope fraction denoted by (-) means natural abundance (i.e., $n_{\text{nat}} = 0.156 \times 10^{-3}$, $(p_{17})_{\text{nat}} = 0.37 \times 10^{-3}$, and $(p_{18})_{\text{nat}} = 2.04 \times 10^{-3}$).

extreme narrowing condition is satisfied. For ease of reference, the relevant expressions are summarized. The relaxation rates are

$$R_D = \frac{3}{8}(2\pi\chi_D)^2(1 + \eta_D^2/3)\tau_D \quad (1)$$

for the D nucleus and for ¹⁷O

$$R_O = \frac{3}{125}(2\pi\chi_O)^2(1 + \eta_O^2/3)\tau_O \quad (2)$$

in which χ_D and χ_O denote the D and ¹⁷O quadrupole coupling constant, respectively. The asymmetry parameters of the D and ¹⁷O field gradient are denoted by η_D and η_O . The intramolecular part of the H-¹⁷O dipolar interaction contribution to the H rate is given by

$$R_{OH}^{\text{intra}} = \frac{35}{3}(\gamma_H^2\gamma_{17O}^2\hbar^2)/r_{OH}^6\tau_{OH} \quad (3)$$

in which r_{OH} is the O-H bond distance.

The correlation times τ_D , τ_O , and τ_{OH} are the time integrals of the correlation functions of the interaction tensors. The relaxation processes are completely intramolecularly determined, and, hence, these correlation times refer to reorientational dynamics only. The principal directions of the interaction tensors of D and ¹⁷O do not coincide. As a consequence, the symmetry of the motion can be investigated by comparing the corresponding correlation times τ_D and τ_O .⁷

The principal axis of the D field gradient nearly coincides with the O-H axis and, hence, with the principal axis of the intramolecular H-¹⁷O dipolar interaction tensor. This, in combination with the small value of the D asymmetry parameter ($\eta_D = 0.135$, gas value), leads to an equality of the effective correlation times for these relaxation mechanisms.⁴ This equality holds irrespective of the details of the motion. One must take into account a small D solute isotope effect, due to the molecular species involved. In the polymer solution this effect is unknown but is taken to be the same as in pure water.⁸ One has

$$\tau_D(\text{HDO}) = (1.05 \pm 0.02)\tau_{OH}(\text{H}_2\text{O}) \quad (4)$$

where the molecular species involved is given in parentheses.

Ab initio quantum chemical calculations show the main factor determining the D field gradient is the O-D bond length. The dependence on bond angle is of minor importance.⁹ A semiempirical connection between χ_D (in kilohertz) and r_{OH} (in angstroms) was proposed:¹⁰

$$\chi_D = \frac{595 \pm 11}{r_{OH}^3} - (390 \pm 9)r_{OH} \quad (5)$$

This relation reproduces experimental and theoretical

results well. A small difference in O-H and O-D bond length has been neglected. Now from eqs 1 and 3-5, one can derive χ_D , r_{OH} , and $\tau_D (=1.05\tau_{OH})$.

A similar procedure to obtain the ¹⁷O quadrupole coupling constant is not feasible. However, for crystal hydrates, different forms of ice, and water vapor, Poplett observed a correlation between χ_O and χ_D .¹¹

$$\chi_O = (38.214 \pm 1.293)\chi_D - (1650 \pm 302) \text{ (kHz)} \quad (6)$$

The ¹⁷O coupling constant may be obtained by inserting χ_D into this relation.

Experimental Section

PAA, degree of polymerization (DP) = 2700, was home synthesized and fractionated.¹² The DP was determined by viscosity measurements, in the presence of 0.01 N HCl, using the Mark-Houwink relation $[\eta] = (0.68 \times 10^{-3})M^{0.5}$ at 302 K.¹² LiOH and CsOH, gold label quality, originated from Aldrich, Milwaukee, WI. Water isotopically enriched in oxygen was obtained from Monsanto Research Corp., Miamisburg, OH, containing 9.9% ¹⁶O, 51.1% ¹⁷O, and 39.0% ¹⁸O. Distilled local tap water was deionized and filtered by a Milli-Q water purification system (Millipore Corp., Bedford, MA). D₂O was obtained from E. Merck, Darmstadt, West Germany. NMR tubes (Wilmad, 10 mm) were heated in a NaHCO₃ solution, heated in an EDTA solution, and then stored for at least 1 week filled with deionized and filtered water. LiPAA and CsPAA solutions were prepared by weight. Concentrations, C_p , are given in number of moles of monomeric units per 55.5 mol of water. The solutions were completely neutralized with alkali to obtain the PAA salts. No excess low molecular weight salt is present in solution. For each type of solute, one solution was prepared with natural water, whereas another solution was prepared using water isotopically enriched in oxygen. Samples containing various amounts of ¹⁷O were obtained by mixing these two solutions. Concentrations and isotopic composition of the samples are collected in Table I.

NMR experiments were performed on a home-built spectrometer equipped with a 2.1-T electromagnet (Bruker). The magnetic field was locked with an external lock probe, using the F resonance in trifluoroacetic acid doped with copper acetate. The temperature was maintained at 298 ± 0.2 K by a fluid thermostat using Fluorinert FC-43 (3M Co., St. Paul, MN). To check any field dependence of the water proton relaxation rates, some experiments were performed on a home-modified Bruker SXP spectrometer (equipped with a 6.3-T superconducting magnet) and a field-cycling instrument. The field-cycling experiment was performed at the IBM T. J. Watson Research Center, Yorktown Heights, NY, by courtesy of Dr. S. H. Koenig.

T_1 measurements were obtained, at least in duplicate, by the inversion-recovery method with an estimated reproducibility of 2%. FIDs were accumulated, while the relative phase of the π and $\pi/2$ pulses was alternated.¹³ The proton relaxation curves were slightly biexponential due to the contribution of the polymer protons. Hence, the collection of data points started when a time interval of 5 times the polymer proton relaxation time has elapsed. Within this interval, the polymer proton reso-

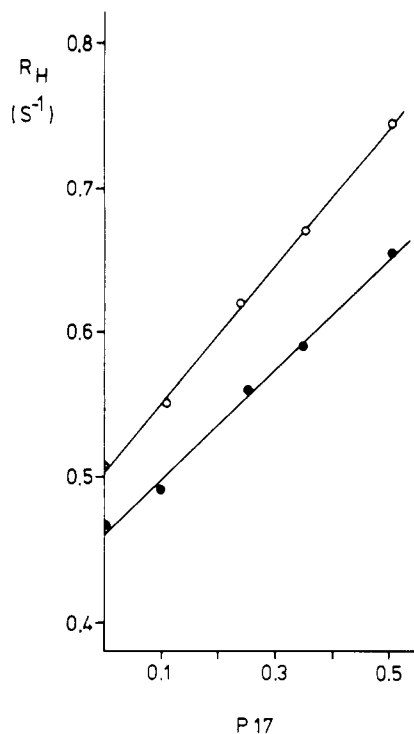


Figure 1. Proton longitudinal relaxation rates, corrected for oxygen isotope viscosity effects, as a function of the ^{17}O mole fraction: open symbols, LiPAA; filled symbols, CsPAA. The lines are drawn according to a linear least-squares fit.

nance is sufficiently relaxed toward equilibrium. A total of 100 data points were fitted to a single exponential by a nonlinear least-squares procedure. No field dependence of the water proton longitudinal relaxation rate in the Larmor frequency range 0.01–270 MHz was observed. Results are collected in Table I.

Results and Discussion

To refer to H_2^{16}O dynamics, oxygen isotope viscosity effects on the relaxation rates are corrected as described before.¹⁴ The corrected ^{17}O relaxation rates (see Table I) are insensitive to the isotopic composition of the samples. This demonstrates the suitability of the correction procedure. Proton relaxation rates are displayed in Figure 1 vs the ^{17}O mole fraction. In view of the observed linearity, one has

$$R_H = R_{HH} + p_{17}R_{OH} \quad (7)$$

in which R_{HH} and R_{OH} denote, respectively, the H–H and H– ^{17}O dipolar interaction contribution to the H relaxation. Values of R_{HH} and R_{OH} , obtained from the fit of eq 7 to the data displayed in Figure 1, are collected in Table II. The intermolecular contribution to R_{OH} is unknown but is taken to be 2% of the total H– ^{17}O interaction contribution, as it is in pure water.⁸ The intramolecular relaxation rates are also collected in Table II.

The absence of any field dependence of the water proton relaxation rate indicates that the frequency dependence of the polymer protons is not transferred to a measurable degree to the water protons. Hence, cross-relaxation between these two proton systems is not significant. Mulder et al. reached a similar conclusion for PMA solutions.¹⁵ However, if frequency-independent cross-relaxation is present, it contributes to the background rate R_{HH} only. This background contribution is not considered here.

In polyelectrolyte solutions, due to the counterion accumulation, a decomposition of the solvent relaxation rates into contributions of polyions and small ions is not fea-

Table II
Parameters Resulting from the Fit of Equation to the Data Displayed in Figure 1 and the Intramolecular H– ^{17}O Dipolar Interaction Contribution

sample	R_{HH} , s^{-1}	R_{OH} , s^{-1}	$R_{OH}(\text{intra})$, s^{-1}
LiPAA	0.504 ± 0.003	0.476 ± 0.011	0.467 ± 0.011
CsPAA	0.461 ± 0.004	0.376 ± 0.015	0.369 ± 0.015

sible.¹ The counterion distribution can be estimated with the simple Oosawa–Manning model.¹⁶ Within this model, the fraction of condensed counterions equals $1 - \xi^{-1}$, in which ξ denotes the linear charge density parameter, ξ is the ratio of the electrostatic energy between neighboring charges on the polymer to the thermal energy kT , $\xi = e^2/4\pi\epsilon_0 A kT$. At 300 K, for completely neutralized PAA (distance between neighboring charged beads, $A = 2.5$ Å) the fraction condensed counterions equals 0.65. This counterion accumulation has an important effect on the solvent relaxation behavior in the vicinity of the chain.¹

In these charged polymer solutions, the solvent relaxation behavior may be described by a two-phase model.¹ In this model, the solvent relaxation rates are decomposed into two contributions. The relaxation rate of water dynamically perturbed by the polyion and its condensed counterions is denoted by R_x^p . For the unperturbed part, in which the remaining counterions are solvated, the relaxation rate is denoted by R_x^u . The labels p, u, and x denote perturbed water, unperturbed water, and the relevant relaxation mechanism, respectively. Now, the experimental rates may be expressed as

$$R_x = \frac{n_h C_p}{55.5} R^p + \left[1 - \frac{n_h C_p}{55.5} \right] R^u \quad (8)$$

in which n_h denotes the number of water molecules dynamically perturbed by a monomeric unit. The conditions for the validity of eq 8 have been discussed in ref 1.

To evaluate the perturbed water relaxation rate, the hydration number, n_h , and the unperturbed water relaxation rate, R_x^u , should be known. The unperturbed water relaxation rate may be estimated from the effect of the uncondensed counterions on the pure water rate.¹ However, at the present polymer concentration, this effect is rather small and can be neglected. Accordingly, the unperturbed water relaxation rate, R_x^u , takes the pure water value. One has $R_D^u = 1.944 \pm 0.004 \text{ s}^{-1}$, $R_O^u = 141.6 \pm 0.5 \text{ s}^{-1}$, and $R_{OH}^u(\text{intra}) = 0.270 \pm 0.011 \text{ s}^{-1}$.⁸ The hydration number, n_h , represents the range of the polyion–solvent interaction. The exact value is unknown, but as a lower limit a value of 6 has been chosen. This is approximately the number of water molecules that are involved to hydrate the charged site and the corresponding fraction condensed counterions. As an upper limit, a value of 15 has been used, i.e., the number of water molecules that are involved to form a monomolecular hydration layer per monomer.

The perturbed water relaxation rates, calculated from eq 8 and the experimental relaxation rates, are collected in Table III. Values of the O–H bond distance, quadrupolar coupling constants, and correlation times are also presented in Table III. The latter values have been obtained by inserting the perturbed water relaxation rates into eqs 1–6. The D asymmetry parameter has been neglected, whereas for ^{17}O the gas-phase value, $\eta_O = 0.75$, has been adopted. It was checked that small variations in intermolecular H– ^{17}O dipolar interaction and the ^{17}O asymmetry parameter do not significantly affect the results collected in Table III. For comparison, the pure water values are $r_{OH} = 0.978 \pm 0.01$ Å, $\chi_D = 254 \pm 7$ kHz, and $\chi_O = 8.1 \pm 0.3$ MHz.^{10,17} In the perturbed phase, for

Table III
Perturbed Water Relaxation Rates, Interaction Constants, and Correlation Times^a

n_h	$R_{OH}^{P(intra)},$ s ⁻¹	$R_D^P,$ s ⁻¹	$R_O^P,$ s ⁻¹	$r_{OH}^P,$ Å	$\chi_D^P,$ kHz	$\chi_O^P,$ MHz	$\tau_O^P,$ ps	$\tau_D^P = (1.05\tau_{OH}^P),$ ps
LiPAA								
6	2.21	14.38	1140	0.985	237	7.4	18	17
15	1.05	6.918	542	0.984	240	7.5	8.5	8.1
CsPAA								
6	1.20	8.753	640	0.977	258	8.2	8.5	8.8
15	0.643	4.668	341	0.977	257	8.2	4.5	4.8

^a The estimated errors in r_{OH}^P , χ_D^P , τ_D^P , and τ_O^P are, respectively, 1, 3, 7, 6, and 14%.

CsPAA no significant change in coupling constants with respect to the pure water values has been detected. For LiPAA, the effects are small and comparable to the estimated error margins.

No significant dependence of the interaction constants on the actual choice of the hydration number in the range $n_h = 6$ –15 has been observed. The calculated interaction constants and correlation times are sensitive to the values of the unperturbed water relaxation rates. These relaxation rates may exceed the pure water values. In this case, the calculated perturbed water O–H bond distance and correlation times decrease, whereas the quadrupolar coupling constants increase toward the pure water values. Another possibility is a reduced H bonding in the unperturbed water phase. This would cause a decrease in unperturbed water O–H bond distance and, accordingly, an increase in the calculated perturbed water O–H bond length. However, the magnitude of the latter effect is unknown and, as an approximation, will be neglected. In this case, the data collected in Table III represent the most conservative estimation.

As discussed in the introduction, neutron-scattering experiments show that water molecules in the vicinity of the polyion are still coordinated to the small ions. Therefore, it may be interesting to compare the perturbed water interaction constants to the values in the hydration shell of the corresponding counterions in a low molecular weight salt solution. Within the Li⁺ hydration shell, the interaction constants take the values $r_{OH} = 0.986 \pm 0.01$ Å, $\chi_D = 236 \pm 7$ kHz, and $\chi_O = 7.4 \pm 0.5$ MHz.⁴ For K⁺ hydration water no change in interaction constants could be detected.¹⁴ The influence of K⁺ on the water structure and dynamics is comparable to the effect of the Cs⁺ ion. In the polyelectrolyte solutions, the perturbed water interaction constants are similar to the hydration water values of the corresponding counterions in a simple salt solution. This indicates the main effect on the coupling constants to be due to the interaction of water molecules with the small counterions. The effect of the polymeric backbone is of minor importance.

The D and ¹⁷O correlation times agree with the values given in the previous NMR investigation on water dynamics in polyelectrolyte solutions.¹ In the latter study, the effect of a possible change in coupling constants with respect to the pure water values has been ignored. On comparing the previous data and the present results, one should note that the data from Table IV in ref 1 refer to an infinitely diluted polyion. The present values refer to a 1 *m* solution. Therefore, a small difference in correlation times between the present and the former results is due to both a small concentration effect and, in case of LiPAA, a small change in coupling constants. However, the small change in coupling constants, as observed for LiPAA, does not affect the previously reported discussion on the dynamics.

The relaxation rates show a dependence on the type of counterion. The rates decrease according to the

sequence Li⁺ > Cs⁺. From the present results it is clear that this behavior cannot be due to a change in coupling constants but has its origin in the correlation times. This counterion specificity, together with the previously discussed effects of excess simple salt, linear charge density, and polymeric side group, shows the water dynamical perturbation to be confined to one or two molecular layers from the macromolecular surface to the bulk.¹ The water reorientational dynamics occurs on the picosecond time scale. No significant difference in correlation times for D and ¹⁷O relaxation has been observed. Accordingly, at this concentration (1 *m*) no anisotropy in reorientational motion could be detected. It should be noted that the correlation times may include an average over several classes of perturbed water, i.e., water near charged sites and water near hydrophobic regions. In this case isotropic reorientational behavior may be observed as a result of compensating effects. At higher concentrations (>2 *m*), significant deviations of the D and ¹⁷O correlation times have been observed.¹ However, even at these relatively high concentrations, the degree of anisotropy remains moderate.

Conclusions

The effects of charged polymers on the water NMR coupling constants have been investigated by a comparison of the intramolecular H–¹⁷O dipolar interaction contribution to the H relaxation rate and D quadrupolar relaxation. For CsPAA no effect has been observed, whereas for LiPAA the effects are on the order of the experimental error margins. These results are comparable to the situation as observed for water molecules within the hydration sheath of the corresponding cations in low molecular weight electrolyte solutions. This indicates the main effect on the coupling constants is the interaction of water molecules with the condensed counterions. This is also supported by high-resolution neutron diffraction experiments, which showed the hydration water molecules to be coordinated toward the small ions. From the present results, it is clear that in the discussion of the solvent dynamics a change in coupling constants is of minor importance.

Acknowledgment. J. R. C. van der Maarel thanks Dr. S. H. Koenig and his co-workers for the hospitality and access to the field-cycling equipment during his visit at the IBM T. J. Watson Laboratory, Yorktown Heights, NY.

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Registry No. LiPAA, 25656-42-2; CsPAA, 35830-08-1; water, 7732-18-5.

¹⁵N NMR Characterization of Multiple Crystal Forms and Phase Transitions in Polyundecanamide (Nylon 11)

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ABSTRACT: Polyundecanamide (nylon 11) was synthesized with 99+% ¹⁵N labeling of the amide nitrogen. Polymer samples were thermally treated to give the stable triclinic α crystal form and the metastable δ' smectic form. The γ form was obtained by precipitation from neat trifluoroacetic acid upon evaporation. ¹⁵N CP/MAS NMR clearly differentiated the samples by chemical shift. Confirming previously reported X-ray and thermal analysis, the α crystal form transforms above 95 °C to the pseudohexagonal δ crystal form. ¹⁵N spin-lattice (T_1) relaxation experiments confirmed decreasing relative mobility in the order $\delta' > \delta > \alpha$ consistent with increasing molecular rigidity and density. Previous studies suggested that the α - δ transition involves the onset of rapid hydrogen bond disruption and re-formation within the crystal lattice above the 95 °C transition temperature. ¹⁵N chemical shift anisotropy (CSA) spectra showed that the hydrogen-bonded amide units remain conformationally rigid in the crystal lattice despite increasing librational motion. Combining ¹⁵N T_1 information with wide-angle X-ray data, a model is presented that accounts for the crystal-crystal transition as well as the relative stability of the three crystal forms.

Introduction

Polyundecanamide (nylon 11) is an important commercial polyamide with curious morphological properties. Evidence of polymorphism has been demonstrated by several workers and found to be dependent on the thermal history of the sample as well as the test temperature.¹⁻⁵ Thermal analysis and X-ray point to two morphologies in samples isothermally annealed below the melting point: the triclinic α form which is stable at temperatures below 95 °C^{2,6} and the δ form which exists at temperatures above 95 °C.⁶ The δ form is unstable at room temperature and reverts to the α form very rapidly on cooling. Samples quenched from the melt, on the other hand, have been shown to crystallize into the kinetically favored but metastable δ' form.^{7,8} Various molecular models have been offered to explain the differences in nylon 11 crystal packing for these three forms. Nevertheless, contradictions remain in the literature concerning the details of packing in the α and δ crystal forms.^{2,4-6}

We undertook a study of the morphology of nylon 11 using X-ray and thermal analysis, first, to examine the effect of the α - δ crystal-crystal transition on the melting behavior and, second, to attempt quantitation of the

relative amounts of each crystal form produced by different thermal treatments.⁹ The transition has been rationalized as a disruption of the layerlike hydrogen bonding between adjacent chains into hydrogen bonds that form and disrupt randomly between chains in a pseudohexagonal array.⁶ The fluctuations of dipoles and hydrogen bonds in nylon 11 is crucial to the validity of this model. Unfortunately, this question cannot be conclusively answered by using the above microscopic and macroscopic techniques, and studies on the electrical properties of nylon 11 gave puzzling results with respect to this question.¹⁰⁻¹⁴

Recently, we have shown that ¹⁵N CP/MAS NMR is a sensitive technique for examining the crystal structure of solid polyamides^{15,16} with chemical shift changes related to specific conformations about the amide group.¹⁷ Isotopic ¹⁵N enrichment of nylon 6 allowed observation of crystalline and noncrystalline resonances accurately and determination of specific T_1 relaxation times.¹⁸ The unique ability of ¹⁵N NMR to directly observe amide behavior at the molecular level in solid polyamides prompted us to prepare isotopically labeled nylon 11 to specifically examine the roles of conformational order and hydrogen bond mobility in the α - δ transition. We report here the