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^{13}C and ^{15}N NMR pH Titration of Poly(vinylamine): A Two-Stage Process Sensitive to Polymer Tacticity

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ABSTRACT: The dependence of the acid dissociation constants on the tacticity of poly(vinylamine hydrochloride), prepared from *tert*-butyl *N*-vinylcarbamate, was determined by ^{13}C and ^{15}N NMR pH titrations. The ^{13}C NMR titration for the CH_2 diads produced typical sigmoidal curves, whereas the CH titration curves were bell-shaped, one for each triad configuration. The ^{15}N NMR pH titration curves were generally sigmoidal. However, the curve for well-resolved *mm* sequence was bisigmoidal, and the break in the curve coincided with the maximum of the corresponding CH titration curve. A two-stage titration process was used to fit the data, yielding $pK_1 = 5.3$, 5.3, and 5.0 for the first stage and $pK_2 = 10.8$, 10.3, and 9.3 for the second stage for the *mm*, *mr*, and *rr* configuration, respectively. A model was proposed to account for this titration process which involves a conformation change of the polymer mediated by hydrogen bond formation near half-neutralization.

Introduction

The acid–base behavior of poly(vinylamine) (PVAm) has been studied extensively by means of potentiometric titration.[1-3] There is general agreement that the unusually strong dependence of p*K* on the charge state of PVAm may be attributed to a neighboring-group effect, but a charge–charge interaction alone does not adequately account for this anomalous effect. The calorimetric titration of PVAm[4,5] was interpreted in terms of a nearest-neighbor interaction that included a hydrogen bond contribution, as originally proposed by Morawetz,[6] but could not provide direct evidence for this effect. Levy and co-workers provided evidence for the role of hydrogen bonding in their NMR relaxation studies of PVAm[7] and the model compounds *meso*- and *rac*-2,4-diaminopentane (DAP),[8] but the configurational effects on p*K* for both the polymer and the models were not investigated.

We have recently shown that the NMR titration of atactic poly(acrylic acid) (PAA) can be used to detect small differences in the p*K* values for the syndiotactic, heterotactic, and isotactic sequences of this polymer.[9] Since that study we have determined, by NMR spectroscopy, the configurational sequence distribution of PVAm.[10,11] On the basis of this information we now report the NMR pH titration of atactic PVAm. The results are analyzed in terms of a two-stage dissociation process, and a model is proposed to account for the calculated dissociation constants.

Materials and Methods

PVAm was prepared from *tert*-butyl *N*-vinylcarbamate as the hydrochloride salt.[12] The model compounds, *m*- and *r*-DAP, were kindly provided as the free base by C. C. Chen and C. G. Overberger (Chemistry Department, University of Michigan). The NMR spectra were recorded on a GE 300 WB spectrometer (NT series) equipped with a 1280 computer and 293c pulse programmer. The ^{13}C NMR spectra of PVAm were obtained with complete proton decoupling on 0.5 M (5% (w/v)) solutions in 10% D_2O at 25 °C containing dioxane as an internal chemical shift reference (66.5 ppm relative to tetramethylsilane). *J*-Modulated spin-echo spectra were acquired by the attached proton test (APT) pulse sequence[13] using $J_{CH} = 125$ Hz to maximize the peak intensity. Pulse angles of 58° (19 μs), repetition rates of 1.5 s, sweep widths of ±7575 Hz, and 16K data points were used to acquire the free induction decays. The ^{15}N NMR spectra of PVAm were obtained with complete proton decoupling on 0.5 M (5% (w/v)) solutions in 10% D_2O at 25 °C. Pulse angles of 75° (30 μs), repetition rates of 3 s, sweep widths of ±1000 Hz, and 2K data points were used to acquire the free induction decays. Ammonium chloride in concentrated HCl was used as an external chemical shift reference (30.31 ppm from ammonia at 25 °C).[14] The pHs were adjusted with concentrated NaOH or HCl and recorded on an Orion research model 701A pH meter with a microcapillary Ingold combination electrode, with no corrections being made for the presence of D_2O. No attempt was made to control the ionic strength during the course of titration, but the ionic strength was generally high.

Data Analysis

The pH titration data were analyzed by the following two-stage ionization process:

$$A \rightleftarrows B + H^+ \tag{1a}$$

$$B \rightleftarrows C + H^+ \tag{1b}$$

The acid dissociation constants are defined in logarithmic form by the extended Henderson–Hasselbach equation.[15]

$$pK_1 = pH - n_1 \log([B]/[A]) \tag{2a}$$

$$pK_2 = pH - n_2 \log([C]/[B]) \tag{2b}$$

The equilibrium mole fraction of the various titration species is given by

$$F_A = [H^+]^{1/n_1}[H^+]^{1/n_2}/Q \tag{3a}$$

$$F_B = (K_1)^{1/n_1}[H^+]^{1/n_2}/Q \tag{3b}$$

$$F_C = (K_1)^{1/n_1}(K_2)^{1/n_2}/Q \tag{3c}$$

where

$$Q = [H^+]^{1/n_1}[H^+]^{1/n_2} + (K_1)^{1/n_1}[H^+]^{1/n_2} + (K_1)^{1/n}(K_2)^{1/n_2}$$

In fitting the data, we assumed that the observed chemical shift is a weighted average of the chemical shifts of A, B, and C as shown by

$$\delta = F_A\delta_A + F_B\delta_B + F_C\delta_C \tag{4}$$

Substitution of the expression for the mole fractions (eq 3) into eq 4 gives a nonlinear formula for δ with seven adjustable parameters (δ_A, δ_B, δ_C, n_1, n_2, K_1, and K_2). For each data set, the equilibrium mole fractions were calculated for iterated values of *n*'s and *K*'s, and eq 4 was compared to the experimental data by a linear least-squares procedure. The seven parameters that gave the minimum error, the sum of the squares of the errors (SSE), are the ones reported in Table I. In one case (*mm* NH_x), where there were insufficient data at an inflection point, the best fit gave an abrupt break in the calculated titration curve. A more consistent curve was obtained by fixing $n_2 = 1$. For the assumption of a single-stage reaction the four

Table I
Two-Stage Acid Dissociation Parameters for PVAm

	CH_2	CH			NH_x
	m	*mm*	*mr*	*rr*	*mm*
pK_1	5.04	5.26	5.33	5.04	5.23
n_1	1.97	1.96	1.63	1.09	1.93
pK_2	10.05	10.77	10.31	9.30	10.49
n_2	2.09	1.18	1.36	1.86	(1.00)[b]
SSE	0.253	0.161	0.043	0.002	0.096
δ_A	36.40[a]	44.60	44.75	44.80	52.32
δ_B	38.93	48.20	46.94	45.16	47.26
δ_C	45.50[a]	44.83	44.08	43.53	45.67

[a] The initial and final δ's fitted to the single-stage dissociation for the *m* CH_2 are 36.41 and 47.21, respectively, and for the *r* CH_2 are 36.96 and 47.54, respectively. The downfield value deviates significantly from the observed chemical shift. [b] Fixed at 1.00 (see Data Analysis).

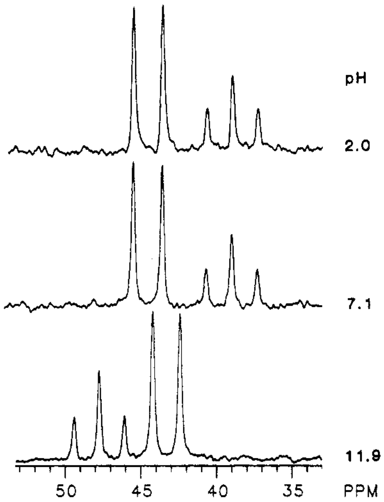


Figure 1. ^{13}C NMR proton-coupled spectra of *m*-DAP at pH 11.9, 7.1, and 2.0.

adjustable parameters were determined in a similar manner.

Results and Discussion

NMR Titration. The ^{13}C NMR spectra of PVAm were recorded in the pH range 2–13. The CH_2 and CH carbon resonances shift downfield with increasing pH, but the CH peaks pass through a maximum and then shift upfield. The CH carbon resonances display triad sensitivity at pH 5 and pentad sensitivity at pH 8. The CH_2 carbon at the latter pH appears as a multiplet. The configurational sensitivity is optimal between pH 8.8 and pH 9.8. In this pH range, the CH carbon shows pentad sensitivity and the CH_2 carbon shows diad sensitivity with partial tetrad resolution.[10,11] Unfortunately, the CH and CH_2 carbon resonances overlap and eventually cross between pH 10.5 and pH 13.0. The model compound *m*-DAP was used to examine this crossing phenomenon. The coupled ^{13}C NMR spectra of *m*-DAP at pH 2.0, 7.1, and 11.9, shown in Figure 1, clearly demonstrate this crossing. The APT experiment[13] was employed in this pH range to identify the CH and CH_2 carbon resonances of the polymer (Figure 2). By this technique the CH_2 carbon (positive peaks) and the CH carbon (negative peaks) may be easily identified in the pH range where their resonances cross, while the spectra obtained with standard proton decoupling are generally uninterpretable.

The assignments of the CH_2 carbon resonances of PVAm are based on our previous report.[10] At pH 8.8, the *m* diad is upfield with respect to the *r* diad. No apparent crossing of these signals has been observed, so we assume that the relationship between the *m* and *r* resonances is preserved throughout the whole pH range. The ^{13}C NMR pH titration is shown in Figure 3 using the average chemical shifts for the CH_2 carbon resonances when the signals exhibit a higher than diad sensitivity. The net downfield shifts due to deprotonation of the ammonium groups for the *m* and *r* resonances are 8.5 and 8.8 ppm, respectively. This result is close to the 9.2 and 9.7 ppm chemical shift

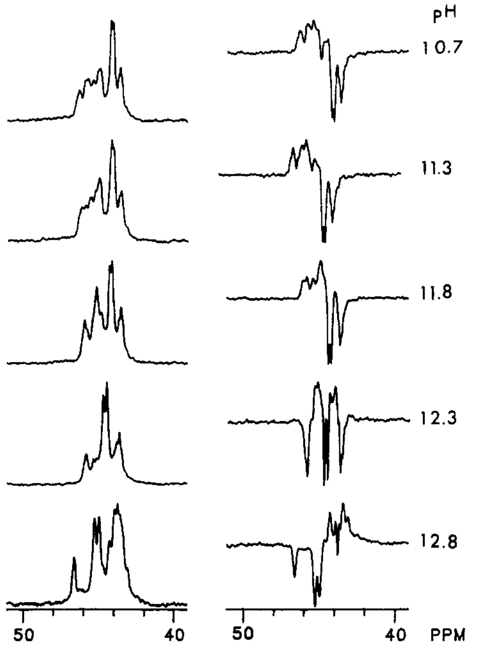


Figure 2. ^{13}C NMR proton-decoupled (left) and corresponding APT (right) spectra for PVAm at pH 10.7, 11.3, 11.8, 12.3, and 12.8.

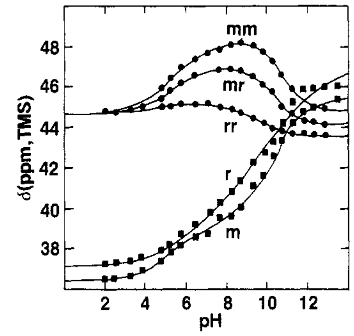


Figure 3. ^{13}C NMR pH titration for the CH_2 and CH carbons of PVAm. Solid curves for the CH triads and *m* CH_2 diads were from a computer fit based on a two-stage titration model (see text for details). The *r* CH_2 diad solid curve was based on a single-stage titration process.

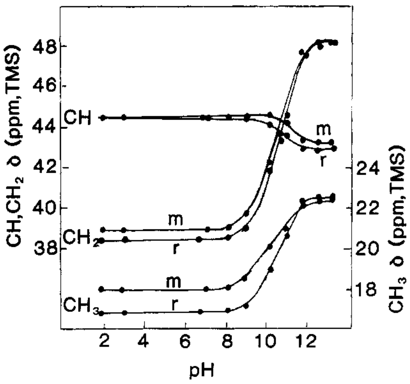


Figure 4. ^{13}C NMR pH titration for the CH_3, CH_2, and CH carbons of *m*- and *r*-DAP.

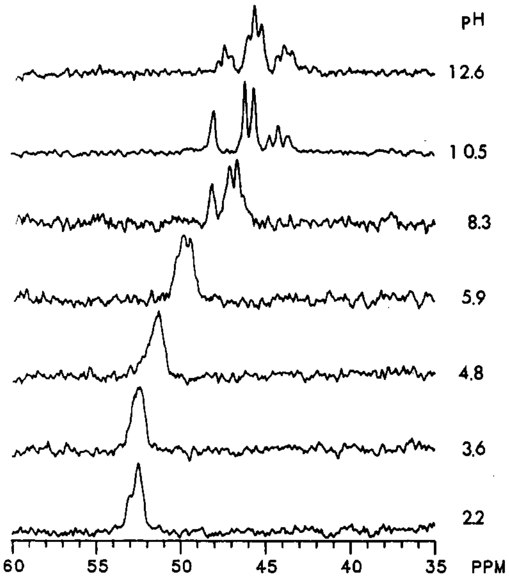


Figure 5. ^{15}N NMR spectra of PVAm at pH 2.2–12.6.

difference for *m*- and *r*-DAP, respectively (Figure 4). The predicted chemical shift difference for a CH_2 carbon due to the deprotonation of two β primary ammonium groups, assuming additivity, is 9.1–9.6 ppm.[16,17]

The assignment[10,11] of the CH resonances for the triad configurations is isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) sequences from downfield to upfield. As above, when higher than triad resolution was observed for the resonances, i.e., pentad resolution at pH 8.2–9.8, the average chemical shifts were used for each triad sequence to plot the titration data. These curves (Figure 3) vary considerably from the corresponding CH titration of DAP (Figure 4), depending on the particular triad sequence. Bell-like titration curves are observed for the *mm* sequence and, to a lesser extent, the *mr* and *rr* sequences. The initial chemical shift at low pH is 44.8 ppm. The maximum chemical shift and corresponding pH for the *mm*, *mr*, and *rr* triads, respectively, are 48.2 ppm (8.68), 46.8 ppm (8.22), and 45.1 ppm (6.45). The final chemical shifts at high pH, for the same triads in the order given, are 44.9, 44.1, and 43.6 ppm. The change in chemical shift for the CH carbon due to the deprotonation of one α and two γ ammonium groups is in principle predictable.[16–19] However, the effect of γ substituents is known to be dependent on conformation. Consequently, these calculations would require both the magnitude of the γ-substituent effect and knowledge of the rotational isomeric states of the polymer.[20]

The amine nitrogen, which is also sensitive to triad configuration,[11] was monitored by ^{15}N NMR during the course of titration. Samples of the ^{15}N NMR spectra of PVAm are presented in Figure 5. The assignments of the ^{15}N resonances are based on our previous report.[11] The configurational assignments in the low-pH range (pH 2–8) are obscure. In this region the average chemical shift and chemical shift width at half peak height were used for all three triads collectively. The average chemical shift for each triad sequence was used in those cases where higher order resolution was observed, e.g., pH 12.6. The titration data for the ^{15}N NMR chemical shifts as a function of pH are shown in Figure 6. The ^{15}N NMR chemical shifts move upfield with increasing pH, in agreement with the results for DAP[8] and other primary amines. The *rr* and *mr* triads are clearly resolved only at pH >9, and the exact nature of the titration curve for these triads is obscured. However, the shape of the *mm* titration curve is unambiguous and typical of a diprotic acid with distinct p*K*'s. It is interesting to note that the break in this titration curve occurs at the same pH as the maximum of the *mm* CH titration curve.

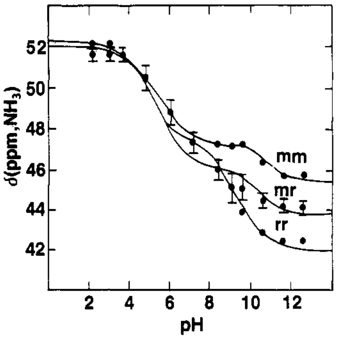


Figure 6. ^{15}N NMR pH titration of PVAm for the *rr*, *mr*, and *mm* configurations. The solid curves are based on a computer fit of the corresponding CH triad data (see text and Figure 3 for details).

Analysis of Titration Data. The nonsigmoidal CH titration curves (Figure 3) and the break in the ^{15}N *mm* NH_x titration curve (Figure 6) suggest a two-stage titration process. Therefore, this model, with each stage conforming to an extended Henderson–Hasselbach equation, was used to fit the data. The best-fit results are reported in Table I.

The *r* CH_2 data failed to yield a well-defined error surface minimum for the two-stage analysis, but this model applied to the *m* CH_2 data resulted in a significantly better fit than was obtained with a one-stage titration. Furthermore, the chemical shift values at the extremes of pH, which are adjustable parameters in both fitting procedures, are in better agreement with the experimental values for the two-stage analysis of the *m* CH_2 data (see note *a* of Table I).

The two-stage titration model was applied to the CH data of each triad and the *mm* NH_x data. There is too much uncertainty in the *mr* and *rr* NH_x data to be useful in these calculations. Each triad dissociation is characterized by four parameters. Where there is a basis for comparison, as found for the *mm* triad, the agreement between the CH and NH_x titration data is quite good. To further test this premise, the CH dissociation parameters, p*K*'s and *n*'s, were used to generate the solid lines for the NH_x titration data shown in Figure 6. The correspondence is good for the *mm* data and reasonable for the *mr* and *rr* data.

The dissociation constants for the fully protonated polymer, based on the CH data (pK_1 = 5.3, 5.3, and 5.0) indicate an unusually strong ammonium acid which appears to be independent of configuration. The dissociation constants for the half-protonated polymer (pK_2 = 10.8, 10.3, and 9.3) are more typical of simple amines (p*K* = 10.72 for isopropylamine), and there is a clear dependence on configuration with acidity increasing in the order *mm*, *mr*, and *rr*. The values of *n* show an unexpected and yet unexplained trend. Large *n* values were anticipated in the acid region, reflecting a strong electrostatic effect, and values near unity were expected in the basic region, indicating a diminished electrostatic effect. This trend is observed for the *mm* triad, but the opposite trend is observed for the *rr* triad.

The empirical analysis of the potentiometric titration data in the literature suggests large nearest-neighbor effects to account for the strong dependence of p*K* on charge state of the polymer.[1,2] In every case, the acid dissociation was treated as a continuous process, even though an

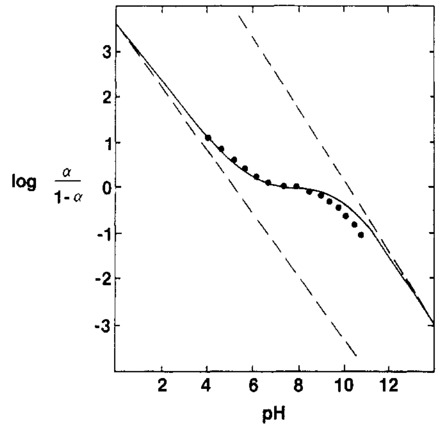
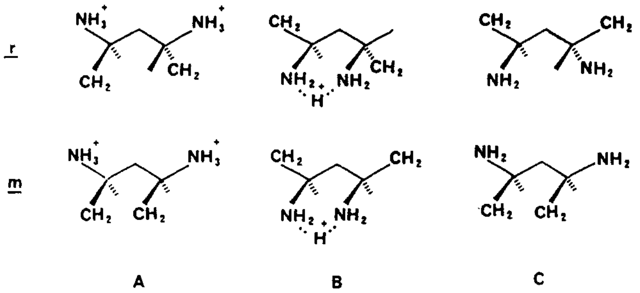


Figure 7. Comparison of the potentiometric titration and NMR titration (solid line for *mr* CH) of PVAm. The dashed lines represent the titration of each stage in the absence of the other stage.

anomalous titration behavior has been inferred. The potentiometric titration data have been described by the extended Henderson–Hasselbach equation with a large n value, but the full titration curve shows a systematic deviation from this equation and is clearly S-shaped.[2,21] This nonlinear behavior is reconciled by our two-stage titration. The potentiometric titration data[22] plotted in Figure 7 (solid dots) are compared to the curve obtained from the two-stage model of the *mr* CH NMR titration (solid line). Clearly, the two-stage model is appropriate for the titration of PVAm.

Two-Stage Dissociation Model. A break in the titration curve as is found for *mm* NH_x (Figure 6) is normally interpreted as an abrubt change in conformation, the classic example being the potentiometric titration of poly(methyl methacrylate).[23] More dramatic effects are observed for copolymers with strongly competing electrostatic and hydrophobic forces.[24,25] We propose a change in conformation in the course of titration of PVAm which is controlled by electrostatic forces and hydrogen bonding. In the following scheme we show the conformational implication of hydrogen bond formation, which is similar to that proposed for DAP,[8] and we assign p*K*'s to the two stages of the titration, pK_1 for A $\rightleftarrows$ B and pK_2 for B $\rightleftarrows$ C.



We expect that the first stage of titration starts with an equilibrium conformation that minimizes electrostatic repulsion (A) and ends with a conformation that maximizes the nearest-neighbor hydrogen bond, NH_2---H^+---NH_2 (B). The conformation change with charge state is reasonably predicted from the theoretical calculations for DAP,[26] and this type of hydrogen bonding contributes substantially (11.4 kcal/mol) to the gas-phase single-proton affinity of DAP compared to *n*-butylamine.[27] This model is further supported by the increase in $\Delta S^{4,5}$ with dissociation, as a consequence of intramolecular hydrogen bonding and concomitant release of hydrogen-bonded water. Finally, the model predicts a relatively strong acid for this stage of dissociation, favored by both electrostatic considerations and hydrogen bond formation, which is consistent with the observed p*K* = 5.2. The fact that the p*K*'s are relatively insensitive to triad configuration may be rationalized by assuming the increased acidity, Δp*K* = 5.5 (7.5 kcal/mol at 25 °C) is due mostly to the electrostatic effect so that the small difference in the energies of the various conformations, due to configuration, is essentially masked.

The second stage of titration starts essentially with the conformation indicated for B and ends at an equilibrium mixture of C conformations, one of which is shown for each configuration. On the basis of the conformational characteristics of poly(vinyl alcohol),[28] which shows little or no tendency to form hydrogen bonds in D_2O, the trans/trans conformation is strongly preferred for the *m* diad and the gauche/gauche is slightly preferred for the *r* diad (as shown above in the model). The trends in p*K* for this stage of the titration are reasonable. First, the electrostatic effects are much smaller; i.e., p*K*'s are more typical of simple ammonium acids. In this case the differences in p*K*'s are due to the difference in energy due to configurations. Second, the B_m state is more stable than the B_r state because of the two equatorially placed CH_2's in the hydrogen-bonded cycle for B_m compared to the equatorial and axial CH_2's for B_r. Therefore, dissociation is slightly favored for the *r* configuration, which is consistent with the observed trend in the configurational dependence on acidity, *rr* > *rm* > *mm*.

In conclusion, the unusually strong dependence of p*K* on the charge state of the polymer for PVAm[2,12] is the consequence of two different dissociating species. The first species, an ammonium group subject to strong electrostatic effects, produces a hydrogen bond upon dissociation and has a p*K* of about 5.2. The second species is an ammonium group subject to weak electrostatic effects which gives up a strong hydrogen bond upon dissociation and has a p*K* range from 9.3 to 10.8 depending upon triad tacticity. The two-stage titration model is consistent with the earlier potentiometric and calorimetric titration of PVAm.

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^{13}C NMR Analysis of Polybutadiene via Cross Polarization and Magic Angle Spinning

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ABSTRACT: Changes in ^{13}C NMR spectra as a function of cross-link density have been investigated for polybutadiene. Increased cross-linking significantly increases the heteronuclear carbon proton dipolar coupling as measured by both ^{13}C T_2 relaxation measurements and combined cross polarization/magic angle spinning measurements (CP/MAS). The CP/MAS measurements provided much higher resolution spectra than T_2 relaxation experiments without the loss of information about low-frequency motions. High-speed MAS was shown to amplitude modulate the static carbon–proton dipolar interaction and frequency modulate the homonuclear proton dipolar coupling. The ability of the MAS to modulate the dipolar coupling is a measure of cross-link density.

Introduction

The analysis of structure in cross-linked polymers can be a very difficult problem. A good example of such a system is polybutadiene (PBd), which, at room temperature, is well above its glass transition point. It is commercially a very important rubber since it is widely used to modify glassy polymers.[1,2] One of the most common ways to measure cross-link density is by swelling in an appropriate solvent and calculating cross-linking from the swelling index using the Flory–Rehner equation.[3] In the case of a pure PBd, this works quite well. However, in a complex rubber modified thermoplastic, such as acrylonitrile–butadiene–styrene resins (ABS) or high-impact polystyrene (HIPS), there are a number of complicating factors such as occlusion levels[4] or grafting[5] that may interfere with the absolute measurement of cross-linking by swelling. In addition, the sample preparation requires separating the grafted rubber from the matrix, so that the rubber properties are not measured directly in the whole polymer.

^{13}C nuclear magnetic resonance (NMR) spectroscopy is a well-known tool for analysis of chemical structure in both liquids and solids. However, rubbery materials, i.e., polymers close to or above their glass transition temperature, are neither true liquid nor true solid. They exhibit some properties of both solids and liquids. High-resolution ^{13}C NMR spectra of these systems can be difficult to obtain since the lines are often very broad, and this broadening gets worse as the cross-link level is increased. It has been reported that useful ^{13}C NMR spectra could be obtained from solid PBd by using standard liquid NMR techniques in solid ABS.[6] The observed lines, however, were very broad unless the sample was spun by using high-speed magic angle spinning (MAS). It has also been reported that NMR relaxation measurements correlate with cross-link density.[7-13]

Although one can use T_2 measurements to make a qualitative analysis of cross-link densities, the extreme broadening in the most highly cross-linked samples does not give sufficient resolution to permit analysis of the cis, trans, and vinyl groups individually. Attempts to improve resolution by obtaining solution-state spectra are pointless since, by definition, a cross-linked sample cannot be dissolved. Swelling with an appropriate solvent might help resolution but would make obtaining reliable T_{2C} information very difficult because the rubber network would be so extended. A reasonable solution to the problems with resolution is to obtain high-resolution ^{13}C NMR spectra in cross-linked rubber by using high-speed magic angle spinning.[14] This, however, eliminates the desired line-width information since the line collapses to an isotropic value.

It is desirable to develop a technique that allows one to use the high resolution obtained with MAS and still be able to observe the effect of cross-linking on low-frequency motions of the rubber, which can be used to explain the physical properties. Measurement of the cross-polarization transfer rate (T_{IS}) is such a technique that is widely applied for NMR of solid systems. It has been difficult to obtain such cross-polarization spectra for rubbers because of poor signal intensity.

It has been reported for adamantane that the static C–H coupling is amplitude modulated by the MAS and that the homonuclear proton coupling is frequency modulated, giving rise to a dependence of transfer rate on the carbon spin locking radio frequency, ω_1. The maximum transfer rates occur when the carbon spin locking radio frequency is offset from the exact Hartmann–Hahn match by integrals of the spinning frequency.[15]

The results reported here will show how one can obtain good CP/MAS spectra of solid rubbers by using a Hartmann–Hahn mismatch. MAS produces some effects on T_{IS} that are not usually observed in glassy polymers. As with adamantane, the magnitude of T_{IS} varies as a function of the difference between carbon and proton ω_1's with maximum transfer rate observed when they differ by a multiple of the spinning frequency. The response of T_{IS}'s to spinning is explained in terms of the proton–carbon

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