Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

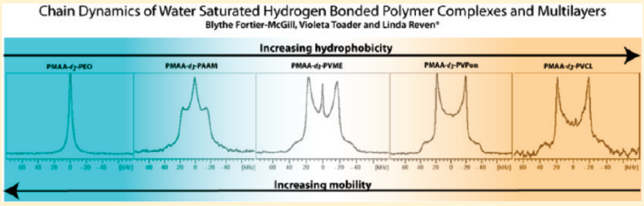
# Chain Dynamics of Water-Saturated Hydrogen-Bonded Polymer Complexes and Multilayers

Blythe Fortier-McGill, Violeta Toader, and Linda Reven*

Center for Self-Assembled Chemical Structures (CSACS/CRMAA), Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

S Supporting Information

**ABSTRACT:** The chain mobility of a series of hydrogen-bonded polymer complexes and multilayers were compared by variable temperature wide-line deuterium NMR spectroscopy. Poly(methacrylic acid), deuterated at the methyl group, PMAA-$d_3$, was complexed with five different hydrogen bond acceptor polymers—poly(ethylene oxide) (PEO), poly(acrylamide) (PAAM), poly(vinyl methyl ether) (PVME), poly(vinylpyrrolidone) (PVPon), and poly(vinylcaprolactam) (PVCL)—as well as with chitosan, where the interaction should be primarily ion pairing. The overall chain mobility of PMAA in its water-saturated complexes was observed to increase in the following order: PVCL < PVPon < chitosan < PVME < PAAM < PEO. For these polymer pairs, the same trend in chain mobility was also confirmed for the first few layers deposited on colloidal silica. The observed chain dynamics correlate well with the reported variation of the critical pH, bilayer thickness, and the permeability for multilayer films of the same polymers. In addition, the extent of chain interpenetration was demonstrated through the effect of a stabilizing primer layer on the chain mobility of the subsequently deposited weaker hydrogen-bonded multilayers.



## 1. INTRODUCTION

Over the past 15 years, multilayer polymer films and hollow capsules formed by the layer-by-layer (LBL) method have been extensively studied. The versatility of polymer interactions can be exploited to create multilayer films that respond differently to pH, temperature, and ionic strength. Most of these studies use the sequential adsorption of polyelectrolytes, and far less work has been done on multilayers based on hydrogen bonding[1] even though H-bonded polymer complexes have been studied for decades.[2] In solution, H-bond donor polymers complex with polymers with H-bond acceptor groups, forming a scrambled egg type structure.[1] Depositing these complexes directly to surfaces via simple precipitation results in poor film quality and uncontrolled thickness, hence the advantage of using the LBL method.[1] The adsorption is self-limiting, which gives control over the film thickness, while the degree of stratification or interpenetration depends on the strength of the complexation.[3] As pointed out in a recent retrospective of the field,[4] the internal structure of polyelectrolyte multilayers has been widely examined, but little work, apart from some NMR studies of supported films[5] and hollow capsules,[6] has been done to correlate the multilayer's macroscopic properties with the underlying chain dynamics. The goal of this study is to assess the chain dynamics of a series of water-saturated complexes and supported multilayers that are primarily stabilized by interpolymer hydrogen bonding. The series of polymers chosen have variable complexation strengths which depend on the relative contributions of several interactions including H-bonding, hydrophobic interactions, and ion pairing. In addition, three of the polymers are known to have thermoresponsive solution properties. The extent to which these properties influence the overall chain dynamics of water saturated complexes and supported multilayers was evaluated.

An earlier study of temperature-responsive polyelectrolyte multilayer capsules found that the calorimetric transitions and variable temperature deuterium NMR spectra of aqueous dispersions of the bulk complexes show the same trends as the hollow capsules.[6] Furthermore, the phase behavior of the polymer complexes in solution is of interest as it controls the amount of material deposited during multilayer growth and the pH response of the supported multilayers.[7] Therefore, we chose to also characterize the chain dynamics of water saturated complexes formed from deuterium-labeled poly(methacrylic acid), PMAA-$d_3$, and a range of hydrogen-accepting polymers that have been used to produce pH responsive multilayer films and capsules. The polymers examined are listed, along with some thermal parameters, in Tables 1 and 2.[8−16] Two of the hydrogen bond acceptor polymers, poly(ethylene oxide) (PEO) and poly(methyl vinyl ether) (PVME), are intrinsically more flexible with low glass transition temperatures, although it is well understood that water behaves as a plasticizer which further lowers the temperature of this transition when present.

The critical pH values at which H-bonded multilayers dissolve are given in Table 2. Sukhishvili et al. defined the critical pH value of H-bonded multilayers films as the pH value at which 50% of the film dissolved after 30 min.[17] The critical pH value is affected

**Received:** December 20, 2010
**Revised:** March 16, 2011
**Published:** March 30, 2011

Table 1. Polymer Properties

| polymer | $T_g$ (°C) | solution critical temperature |
|---|---|---|
| PMAA | 228[8] | |
| PVPon | 177[9] | |
| PVCL | 145[10] | 31–37 °C[12] LCST |
| PEO | −55[9] | |
| PVME | −31[8] | 35 °C[13] LCST |
| PAAM | 165[8] | 20–25 °C[14] UCST for the PAAm/PAA network |
| chitosan | 203[11] | |

Table 2. Critical pH and Bilayer Thickness of PMAA Multilayers

| PMAA complex | critical pH | bilayer thickness (nm) |
|---|---|---|
| PEO | 4.6[15] | 20[16] |
| PAAM | 5.0[1] | 7[1] |
| PVME | 6.2[16] | 15.6[16] |
| PVPon | 6.4[1] | 4[16] |
| PVCL | 6.95[16] | 4.8[16] |

by the hydrophobicity of the polymers and can vary with temperature.[16,17] It is well-known that hydrogen bonds are weakened as the temperature is increased while hydrophobic interactions are strengthened, as demonstrated for polymer complexes using viscosity and turbidity measurements.[18] The balance among stabilization interactions affects the solubility of polymers in water. Certain hydrophobic polymers will precipitate out of solution above the lower critical solution temperature (LCST) as the hydrogen-bonding interactions with the water weaken with increased temperatures. On the other hand, more hydrophilic polymers can have an upper critical solution temperature (UCST) that is the temperature above which the polymer will dissolve in water. The polymers included in this study with known thermoresponsive solution properties are PVME and PVCL which have similar LCSTs while a poly(acrylamide) (PAAM)/poly(acrylic acid) (PAA) complex has an UCST at an ambient temperature as shown in Table 1. Even for polyelectrolyte supported multilayers it has been illustrated that hydrophobic interactions must also be considered to explain the stability of films formed by the LBL addition.[19] Therefore, in the case of polymer multilayer films, the temperature and pH value at which the films will dissolve can be controlled by modifying the hydrophobicity of the component polymers. For biomedical applications, the dissolution of the polymer multilayers films is desired to be close to the physiological pH value and temperature. After acquiring scanning electron microscopy (SEM) images of the capsules produced from PMAA supported multilayers to validate the LBL growth, we examined the chain dynamics of the series of water-saturated PMAA complexes and supported multilayers using $^2$H NMR.

## 2. MATERIALS AND METHODS

**Materials.** Poly(methacrylic acid) (PMAA; $M_w$ 9.5 kDa) as a 30 wt % solution, poly(ethylene oxide) (PEO; $M_w$ 300 kDa), poly(vinyl methyl ether) (PVME $M_w$ 1.5 kDa, determined independently by mass spectroscopy) as a 50 wt % solution, poly(acrylamide) (PAAM; $M_w$ 10 kDa) as a 50 wt % solution, poly(vinylpyrrolidone) (PVPon; $M_w$ 29 kDa), and chitosan oligosaccharide lactate were all purchased from Sigma-Aldrich and were used as received. Poly(vinylcaprolactam) (PVCL; $M_w$ 1.8 kDa) was purchased from Polymer Source and was used as received. The 70–100 nm, 40–41 wt %, $d$ = 1.29–1.32 g/mL, pH 8.5 Snowtex colloidal silica was provided by Nissan Chemical. The 1 M HCl was purchased from Aldrich or prepared from a 48 wt % HCl solution purchased from Fisher. The glacial acetic acid, sodium acetate, and monobasic and dibasic sodium phosphates were all purchased from Fisher. Methyl bromoacetate, iodomethane-$d_3$, triphenyl phosphite, paraformaldehyde, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (97%) (ABAP), and anhydrous dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich and were used as received. The Milli-Q water had measured resistance of 18.2 Ω. Deuterium depleted water (99.9%) was purchased from Sigma-Aldrich.

**Polymer Synthesis.** *Monomer Synthesis.* Methacrylic acid-$d_3$ sodium salt was obtained by basic hydrolyses of its corresponding methyl ester that was synthesized following the procedure reported by Ayrey and Wong[20] (Scheme 1, see Supporting Information). Methyl bromoacetate was treated with triphenylphosphine in ethyl acetate at 80 °C to give carbomethoxymethyltriphenylphosphonium bromide, as a white precipitate, in 70% yield. After separation, this salt was deprotonated with 2 N aqueous NaOH giving the carbomethoxymethylenetriphenylphosphorane that after treatment with iodomethane-$d_3$ in dry dichloromethane, at 40 °C, afforded the deuterium-labeled methyl-$d_3$(α-carbomethoxymethyl)triphenylphosphonium iodide (72% yield). This iodide salt was reacted with paraformaldehyde via its corresponding phosphorane formed *in situ* in the presence of NaH, to give methyl methacrylate-$d_3$ in 69% yield.This subsequently was subjected to hydrolysis, under basic conditions, to give the desired methacrylic acid-$d_3$ sodium salt in 91% yield. (Details regarding the reaction conditions are given in the Supporting Information.)

*Polymer Synthesis.* In a typical polymerization reaction, a 10% aqueous solution of methacrylic acid-$d_3$ sodium salt (with a pH 9) was transferred to a Schlenk tube charged with the desired amount of the initiator (ABAP). The reaction mixture was degassed via 3–4 thaw–pump cycles, then the tube was closed, and the polymerization was performed at 60 °C for 18 h. After cooling to room temperature, the contents of the tube were poured into a large amount of ethanol, and the white precipitate formed was separated by filtration and washed with cold ethanol. A second purification by precipitation from ethanol was performed followed by extensive dialyses against water. Finally, the polymer was dried under vacuum at 45 °C.

*GPC Analysis.* The $M_W$ of PMAA-$d_3$ was calculated to be 22 kDa with a polydispersity of 1.97 and a $dn/dc$ value of 0.164 using a Polymer Laboratories PL-GPC 50 plus. This is a triple detection instrument, with two PL aqua gel–OH 7.5 mm i.d. columns and a guard column. The instrument was calibrated with Viscotek PEO 22 K Narrow Standard at a flow rate of 1 mL/min and at a temperature of 30 °C. The mobile phase used was a 0.1 M pH 9 phosphate buffer. (The retention time traces are provided in the Supporting Information.)

**Sample Preparation.** *Bulk Complexes.* The typical concentration of the initial polymer solution was 4 mg/mL dissolved in 20 mM pH 3.8 acetate buffer. The pH values of these solutions were adjusted using either 1 M HCl or 1 N NaOH if required to obtain a measured value of pH 3.8. The complex suspensions were formed upon the dropwise addition of 10 mL of the PMAA solution to 10 mL of the hydrogen accepting polymer solution, from which a white precipitate was formed immediately. The pH of these complex suspensions was further adjusted to a constant value of pH 1.2 using 1 M HCl. The complex suspensions were concentrated by centrifuging at 7K rpm for 2 min. The supernatant was decanted, and the complexes were dried under vacuum for 24 h.

For the preparation of the chitosan–PMAA complex formed primarily through electrostatic interactions the pH values of the initial polymer solutions were chosen to optimize the respective degrees of ionization. A high degree of ionization of chitosan's primary amine, $\mathrm{p}K_a$ = 6.5, also promotes solubility as the commercial preparation of

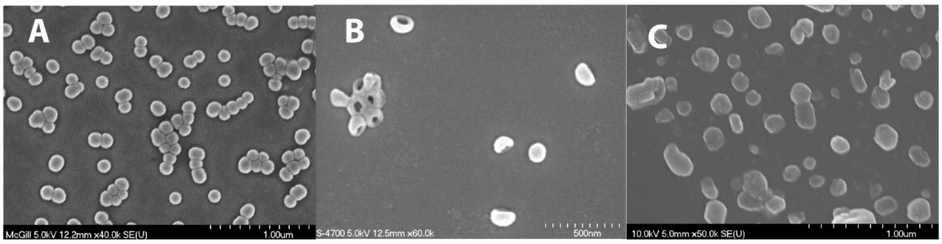


**Figure 1.** Scanning electron microscopy images of (a) template colloidal silica particles 70−100 nm, (b) (PVPon/PMAA)$_{5.5}$ capsules, and (c) (PVPon/PMAA)$_1$(PEO/PMAA)$_{4.5}$ capsules.

chitosan from chitin leaves ~10% acetyl groups untransformed. The chitosan was dissolved in a pH 3.5 200 mM acetic acid while the PMAA was dissolved in pH 6.5 100 mM phosphate buffer. The PMAA solution was added dropwise to the chitosan solution, from which a white precipitate was formed immediately. The measured pH value of this suspension was ~pH 5. The suspension was allowed to settle overnight, decanted, and dried in a vacuum oven for 24 h.

For the pH study of the PEO−PMAA-$d_3$ (2:1, mole ratio) complex one was prepared and suspended in a pH 2 solution while the other was prepared at pH 3 and suspended in a pH 5 20 mM acetate buffer solution overnight.

*Multilayers.* First, 0.94 mL of the Snowtex suspension, which is equivalent to 0.5 g of the colloidal silica, was centrifuged and resuspended in the pH 3.8 20 mM acetic acid buffer, a total of 3 times, to ensure that the surface was sufficiently protonated, as the pH value of the stock silica suspension is pH 9. The hydrogen-accepting polymer, either PEO, PVME, PVPon, or PVCL, was then added as a 20 mL aliquot with the concentration of 0.45 mg/mL in 20 mM pH 3.8 acetate buffer solution and mixed for 5−12 h to ensure sufficient adsorption. The suspension was then washed three times with the 20 mM pH 3.8 acetate buffer with sequential centrifuging at 5K rpm for 1−10 min and resuspending by vortexing at 1K rpm for 1−12 h. This was followed by the addition of 10 mL of the 1 mg/mL PMAA-$d_3$, 20 mM, pH 3.8 acetate buffer solution. These solutions were washed three times followed by the addition of 20 mL of the corresponding hydrogen-accepting polymer solution. These supported multilayers were then washed and dried under vacuum for 24 h.

For the PVPon primed PEO supported multilayers the above conditions were used where the PVPon was added first followed by the PMAA while subsequent layers alternated between PEO and PMAA until the specified layer was reached. After the desired layer was obtained, the samples were concentrated by centrifugation. (Evidence of the layer growth using $^{13}$C solid-state NMR and thermogravimetric analysis are shown in the Supporting Information.)

For the PAAM-supported multilayers little to no polymer adsorption was observed for the above conditions so higher concentrations and lower pH values were used, where 0.47 mL of the silica suspension was washed three times with a pH 2.9 HCl solution, followed by the addition of 5 mL of the 4.4 mg/mL pH 2.4 PAAM solution. After three washing steps 10 mL of the 2.0 mg/mL pH 2.1 PMAA-$d_3$ solution was added and washed. After the second PAAM layer was added and washed the concentrated suspension was dried under vacuum for 24 h.

For the chitosan multilayers a more concentrated solution was used for convenience, where 10 mL of the 1 mg/mL chitosan in 20 mM pH 3.8 acetate buffer was added to 0.5 g of washed silica. Also, a total of five layers were added as opposed to the three layers that were used for the other polymer pair multilayers as these multilayers resuspended more rapidly.

*Capsules.* The supported multilayers were added dropwise to a 0.5 M HF solution and allowed to stir for at least 2 h. The suspension was then washed with the 20 mM pH 3.8 acetate buffer solution, by centrifugation at 6.6K rpm for 5−45 min, decanting, and subsequent resuspension. The supernatant was discarded into a 2 M calcium chloride solution, where the excess fluoride ions form an insoluble calcium fluoride salt. The washing steps were repeated until the supernatant no longer formed a white precipitate upon addition to the calcium chloride solution. (The effects of long-term storage of the capsules in 0.5 M HF are shown in the Supporting Information.) *Caution: care must be taken when using and storing HF.*

*NMR Sample Preparation.* For PEO, PAAM, PVME, PVPon, and PVCL, PMAA-$d_3$ coated silica, ~90 mg, with ~6 wt % polymer multilayer was placed in the 5 mm sample holder followed by the addition of 1 drop, ~0.015 mL, of deuterium depleted water whose pH value was adjusted to pH 1.3 using 48 wt % HCl. For the bulk complexes, ~20 mg of sample was added to the sample holder with the addition ~0.03 mL of the acidic deuterium water, resulting in ~40 wt % bulk complex which is more concentrated in terms of polymer content than the 5 wt % supported multilayers. For the chitosan-supported multilayers pure deuterium depleted water was used. For the PVPon primed PEO multilayers deuterium depleted water was not used, as these multilayers were not dried so they were therefore suspended in the pH 3.8 acetic acid 20 mM buffer solution.

**Characterization.** *$^2$H NMR.* Solid echo deuterium spectra were recorded on a Bruker 600 spectrometer operating at 600.14 MHz for $^1$H and 92.1255 MHz for $^2$H that supported 5 mm outer diameter sample holders, with a sample volume of ~0.17 mL. The solid echo sequence was used with a $^2$H 90° pulse of 2.9 $\mu$s, an echo delay of 24 $\mu$s, and a recycle delay of 0.2 s, with 2868 scans used for the water saturated complexes and either 4000, 32 000, or 64 000 scans used for the supported multilayers. Variable temperature $^2$H NMR of $D_2O$, whose melting point is 3.8 °C, was used to equate the temperature to an exact value while the change in temperature was monitored by the $^{207}$Pb shift in $PbNO_3$ where the temperature dependence of the shift was calibrated by Beckmann and Dybowski.[21]

*NMR Line Shape Simulations and Fits.* A series of 36 basis spectra were simulated by a modified FORTRAN code provide by Wittebort et al.[22] Details of the modification are provided elsewhere.[6] The simulation input parameters included a 180° pulse length of 5.8 $\mu$s, an echo delay of 24 $\mu$s, a line broadening of 1000, a spectral half-width of 150 kHz, and a reduced quadrupole coupling constant of 51 kHz (where a detailed explanation of the methyl group's 3-fold reduction of the quadruple coupling constant is shown in the Supporting Information). The rates were varied from 400 to $10^{10}$ jumps/s (Hz), with 12 rates each for the slow (0.4−10 kHz), intermediate (15−150 kHz), and fast (200−$10^7$ kHz) groupings of motion. The weighting factors of each of the simulated spectra were found by finding the minimum of a scalar function of several variables, starting at an initial estimate using MATLAB (The Mathworks, Inc., Natick, MA). This is generally referred to as unconstrained nonlinear optimization. The absolute values of the variables were taken so that the positive weighting factors of a series of spectra could be obtained.

*SEM.* The suspension was deposited as a liquid drop on a glass cover slide attached, using carbon tap, to a pin style SEM mount, and allowed

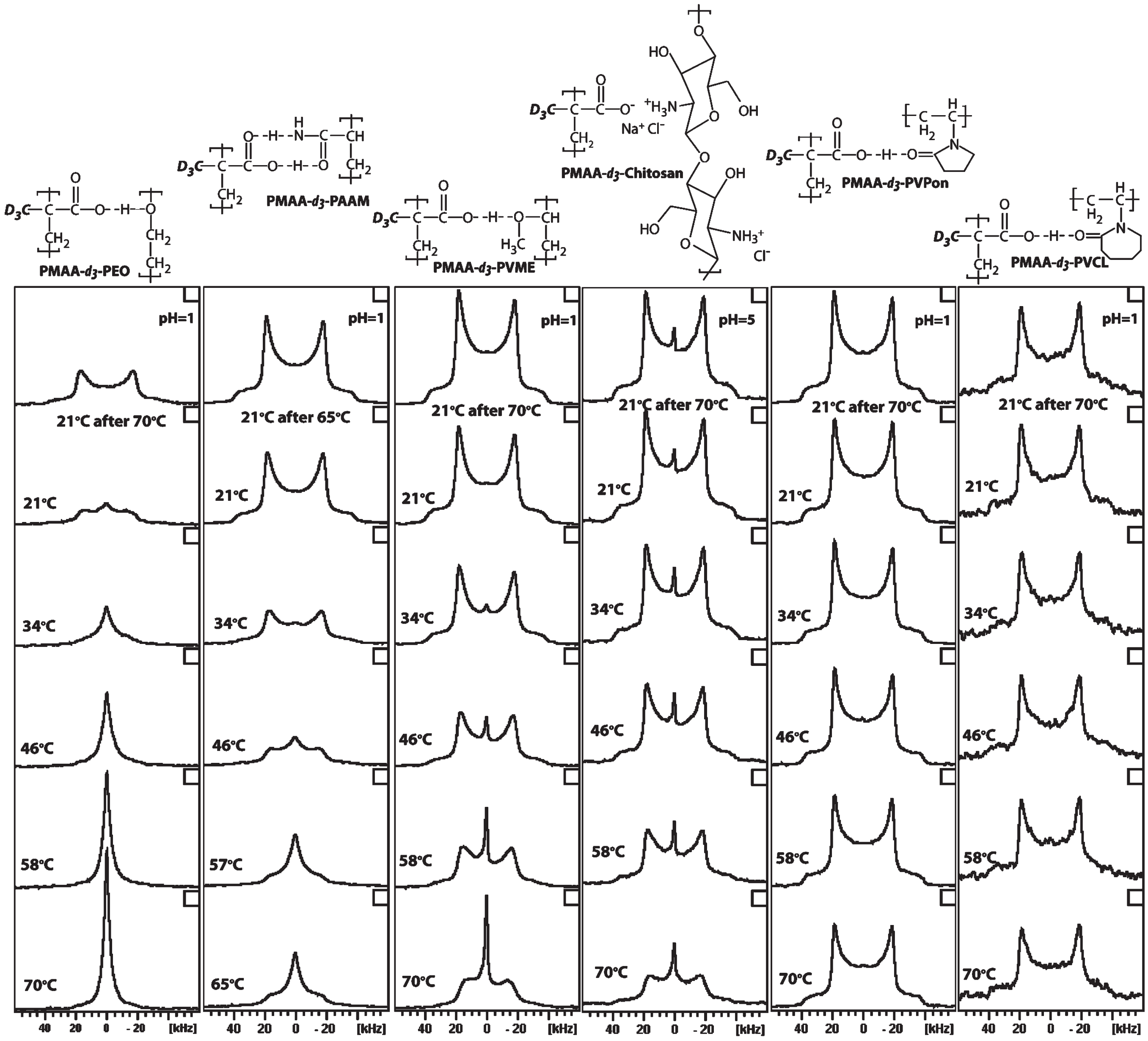


**Figure 2.** Variable temperature $^2$H NMR of ∼40 wt % PMAA-$d_3$ complexes saturated with acidic deuterium depleted water, with the exception of the chitosan complex which was saturated with untreated deuterium depleted water.

to dry overnight. The sample was then coated with a gold/palladium mixture using a Hummer VI Sputtering System for a coating time of 3−4 min. A Hitachi S-4700 FE-SEM was used with a specimen spacing of either 12.5 or 5 mm from the detector and a current of either 2 or 10 $\mu$A with a voltage of either 2 or 5 kV.

## 3. RESULTS AND DISCUSSION

An indication of the large variation in the chain dynamics and hence the mechanical properties of the H-bonded polymer multilayers with different acceptor/donor combinations can be seen when hollow capsules are prepared. Figure 1 displays the SEM images of the template 70−100 nm silica colloidal particles (Figure 1A), the capsules formed from multiple bilayers of the strongly interacting PVPon/PMAA pair of polymers (Figure 1B), and the capsules formed with one PVPon/PMAA bilayer followed by multiple bilayers of the weakly interacting pair of polymers PEO/PMAA (Figure 1C). Stable PEO/PMAA capsules could only be prepared by depositing a primer layer of another hydrogen bond acceptor polymer since PEO adheres poorly to the silica surface, as was also shown by Kozlovskaya et al.[23] The SEM images indicate that the PVPon primed PEO/PMAA submicrometer capsules (Figure 1C) are softer as they collapse and lose their spherical shape upon drying whereas some of the capsules produced from the strongly interacting PVPon/PMAA (Figure 1B) layers only partially collapse. Images of the capsules were only achieved when the final capping layer was the hydrogen-accepting polymer. When the hydrogen donor/PMAA polymer was the capping layer, excessive aggregation occurred due to the low pH conditions of the core dissolution process. Even during layer addition it was noted that the colloids aggregated more when PMAA was the capping layer; therefore, all the

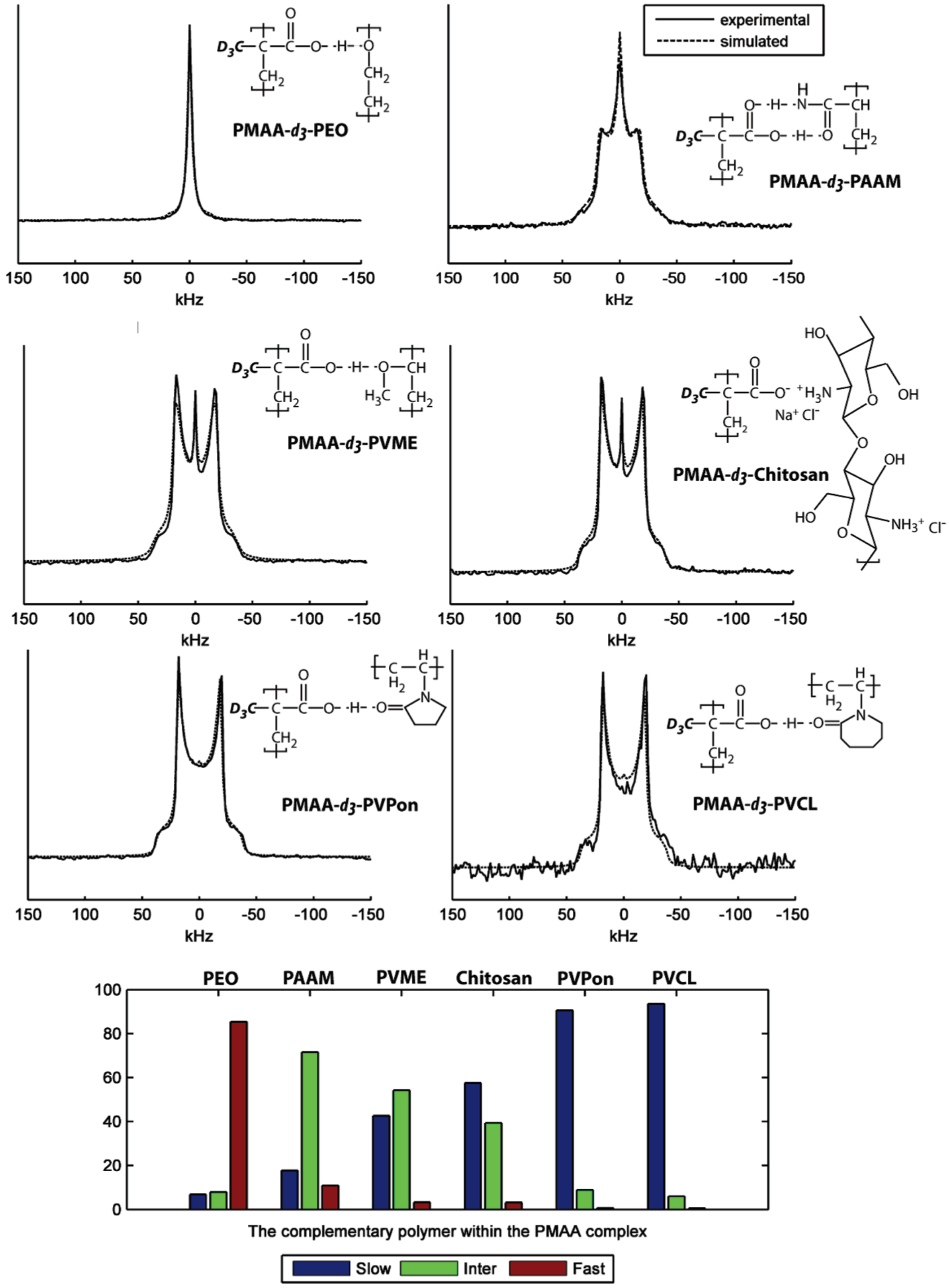


**Figure 3.** Fits of $^2$H NMR spectra of ~40 wt % PMAA-$d_3$ complexes saturated with deuterium depleted water, at 46 °C illustrating the contribution of the slow, intermediate, and fast chain motion, which is defined as (0.4−10 kHz), (15 −150 kHz), and (200−$10^7$ kHz), respectively.

supported multilayers and capsules studied were terminated with the hydrogen-accepting polymer layer.

The $^2$H NMR spectra of the series of PMAA complexes saturated with acidic water over a temperature range of 21−70 °C are presented in Figure 2. The onset of chain mobility with increasing temperature is indicated by the averaging of the Pake pattern to an isotropic peak. In the case of the weak PEO/PMAA complex, a significant isotropic component is present even before heating and the broad component vanishes upon warming just above room temperature. The PAAM and PVME complexes display an isotropic component with moderate heating but, unlike the PEO complex, retain broad components at the highest temperatures examined. The chitosan−PMAA polyelectrolyte complex displays an onset of motion with frequencies in the intermediate rather than fast regime as signaled by the gradual attenuation of the Pake pattern intensity. Finally, for the polymers that form the strongest complexes with PMAA, PVPon, and PVCL, the PMAA chain motion remains restricted with no significant change in the $^2$H Pake pattern line shapes with heating. This concurs with AFM measurements of a single PVPon/PMAA capsule taken at a pH value of 2 that showed an elastic modulus typical of a glassy state.[24]

The trend in the chain mobility is presented more quantitatively through line-shape simulations of all the complexes at 46 °C (Figure 3). The contributions of the fast (200–$10^7$ kHz), intermediate (15–150 kHz), and slow (0.4–10 kHz) motional frequencies to the line shapes are summarized by the bar graph at the bottom of Figure 3. Although the diffusion type model used has been shown to be appropriate for motionally heterogeneous type systems such as polymers,[25] a series of three spectra with different echo delay times were fit with the same distribution of jumping rates, which were simulated with the corresponding echo delay time (see Supporting Information, Figure S6). This adds validity to the model used and shows that the distribution of jumping rates determined from the fits is representative of the relative amounts of the polymer in these motional regimes. Only the PEO and PAAM complexes, whose complexation with PMAA contains a minimal contribution of hydrophobic interactions, display a significant amount of the fast motion component. Considering the slow motion contribution only, the complexes have the following order: PEO < PAAM < PVME < chitosan < PVPon < PVCL. This trend exactly mirrors the order of increasing critical pH values for the dissolution of the multilayer films composed of the same polymer pairs (Table 2). The chain mobility of chitosan, which forms a complex with PMAA based primarily on electrostatic interactions, is intermediate between the weak, hydrophilic, and strong, more hydrophobic H-bonded complexes. It is reasonable to assume that the chitosan/PMAA complex is primarily stabilized by electrostatic interactions as it is well-known that this interaction is stronger than both hydrophobic interactions and hydrogen bonding.[26] Also, the pH value was optimized to favor the electrostatic interactions between PMAA

**Table 3. Temperature Ranges for the Averaging of the $^2$H NMR Broad Component**

| PMAA complex | temperature range (°C) |
|---|---|
| PEO | 15–25 |
| PAAM | 34–46 |
| PVME | 60–70 |
| chitosan | 60–70 |
| PVPon primed PEO ML | 65–75 |
| PVPon | >80 |
| PVCL | >80 |

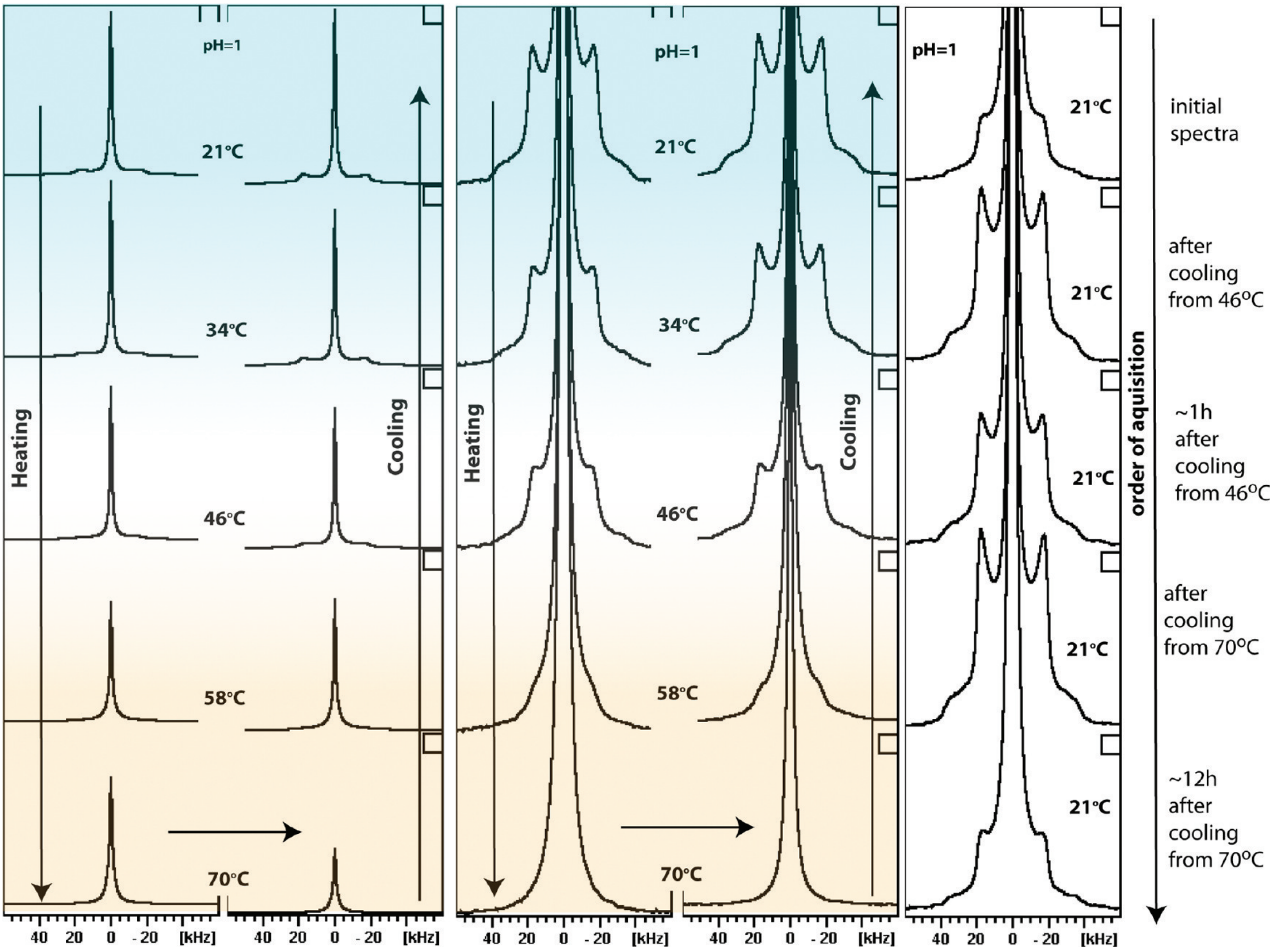


Figure 4. Variable temperature $^2$H NMR of ~40 wt % bulk PMAA-$d_3$ saturated with acidic deuterium depleted water. Left side: the heating and cooling set showing the full intensity of the isotropic peak. Middle: expansion of the spectra to show the small Pake component. Right side: $^2$H NMR spectra at 21 °C acquired at different times after the heating cycle. The samples were equilibrated for 10 min at each temperature unless otherwise specified.

and chitosan (pH 4.5) as no precipitate was observed under the conditions used for the H-bonded complexes (pH 1.2).

The relative chain mobilities of acid saturated bulk complexes are also correlated with other properties of H-bonded polymer multilayers that have been recently reported in the literature. The bilayer thickness in the linear growth regime on solid substrates and the permeability of the multilayer membranes both decrease with increasing critical pH values.[1] (Table 2) This documented bilayer thickness correlates with the amount of chain mobility, where more compact layers result in restricted chain motion and corresponds to higher reported critical pH values,[1] all of which reflects the increased quantity of interpolymer hydrogen bonds. Likewise, it has been shown in the literature that the weakly H-bonded multilayer films with loosely packed, mobile chains are more permeable to small molecules.[16] The diffusivity of dye molecules through 10-layer films deposited on a porous membrane decreased in the following order: PMAA/PEO, PMAA/PVME, PMAA/PVPon, and PMAA/PVCL with the ratio 380:40:5:1.[16] The thermoresponsive multilayers, PMAA/PVME and PMAA/PVCL, display an irreversible increase in diffusivity when the temperature approaches the LCSTs of PVME and PVCL. Rather than being due to more chain mobility as occurs for PEO at elevated temperatures, the increase in permeability is attributed to deswelling of noncomplexed PVME or PVCL chain segments and the opening of voids within the multilayer film.[16] In the case of the bulk complexes, the temperature response of PVME and PVCL is largely unobservable due to more complete complexation. Furthermore, the temperature response of the noncomplexed PVME or PVCL chain segments would not be expected to have a large effect on the $^{2}$H NMR spectra of the PMAA-$d_3$.

The temperature ranges over which the Pake patterns collapse are summarized in Table 3. In bulk solid polymers, this averaging is normally associated with the glass transition temperature where the "NMR $T_g$" occurs $\sim$40 deg above the $T_g$ measured by calorimetry due to the different time scales of the two methods (MHz versus sub-Hz frequencies).[27] For polyelectrolyte complexes and hollow capsules, the collapse was proposed to be a measure of the amount of thermal energy required to simultaneously break enough linkages to free chain segments and allow solvation, as the endotherms detected by DSC occur in the same temperature range as the onset of chain motion as detected by $^{2}$H NMR.[6] For the H-bonded complexes, disassociation versus enhanced mobility of the intact complex needs to be considered. PAAM has an UCST around 20−25 °C when complexed to PAA, a property used to form negatively thermoresponsive gates via reversible zipper type hydrogen-bonding interactions.[14] The onset of fast motion at 34−46 °C of the PMAA−PAAM complex presumably arises by the same process though in higher temperature range due to the stronger complex formed by PMAA with PAAM as compared to PAA. However, the PEO, PVME, PVPon, and PVCL complexes with PMAA are known to stabilize at higher temperatures due to increasing hydrophobic forces,[18] and the collapse may indicate an overall increase in the dynamics of the complex itself arising from the increasing rate of exchange between intra- and interpolymer hydrogen bonds.

Even in dry solid PAA−PEO complexes, $^{13}$C chemical shift studies show that there is slow exchange between intrapolymer H-bonds (PAA dimers) and interpolymer H-bonds.[28] These studies also revealed that heating favors self-association of PMAA over complexation with PEO; that is, the population of the intrachain PMAA hydrogen bonded dimers increases relative to the interchain hydrogen bonds of the complex.[28b] The PMAA intrapolymer hydrogen bonding was observed to be stronger and better ordered in the PEO complex than in pure PMAA. The large difference in mobility between PEO and PMAA in the solid complex was proposed to facilitate breakage of the interpolymer hydrogen bonding.[28b] For the PEO/PMAA-$d_3$ complex it can be seen in Figure 2 that the spectrum acquired at room temperature after the heating cycle (first spectrum) shows a stronger powder pattern, suggesting that PMAA has rearranged into conformations with reduced degrees of motion.

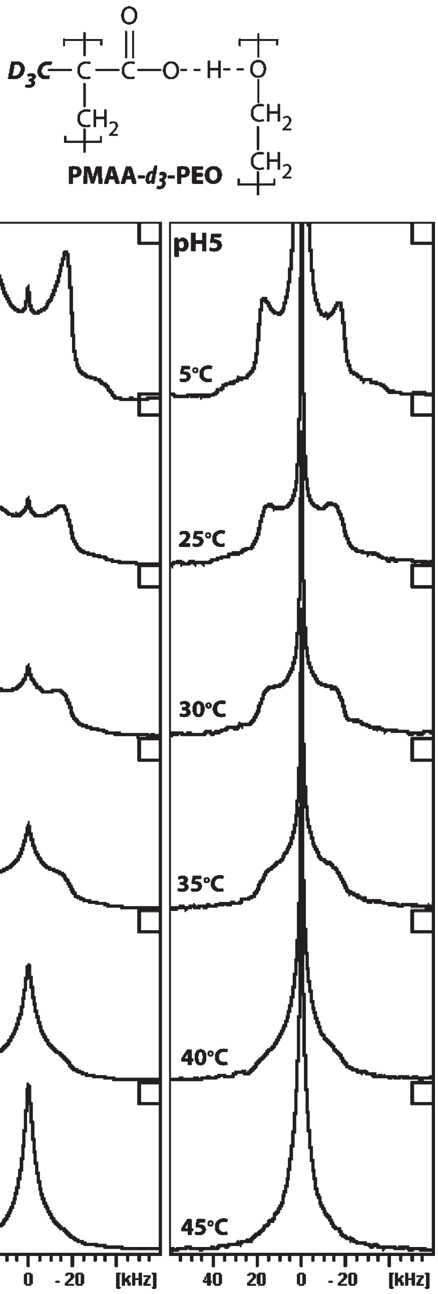


Figure 5. Variable temperature $^{2}$H NMR of a PEO−PMAA-$d_3$ complex prepared and suspended in a pH 2 solution (left) and prepared at pH 3 and suspended overnight in a pH 5 20 mM acetate buffer solution (right).

As a control, pure PMAA-$d_3$ was mixed with the same proportion of acidic deuterium depleted water as in the hydrated

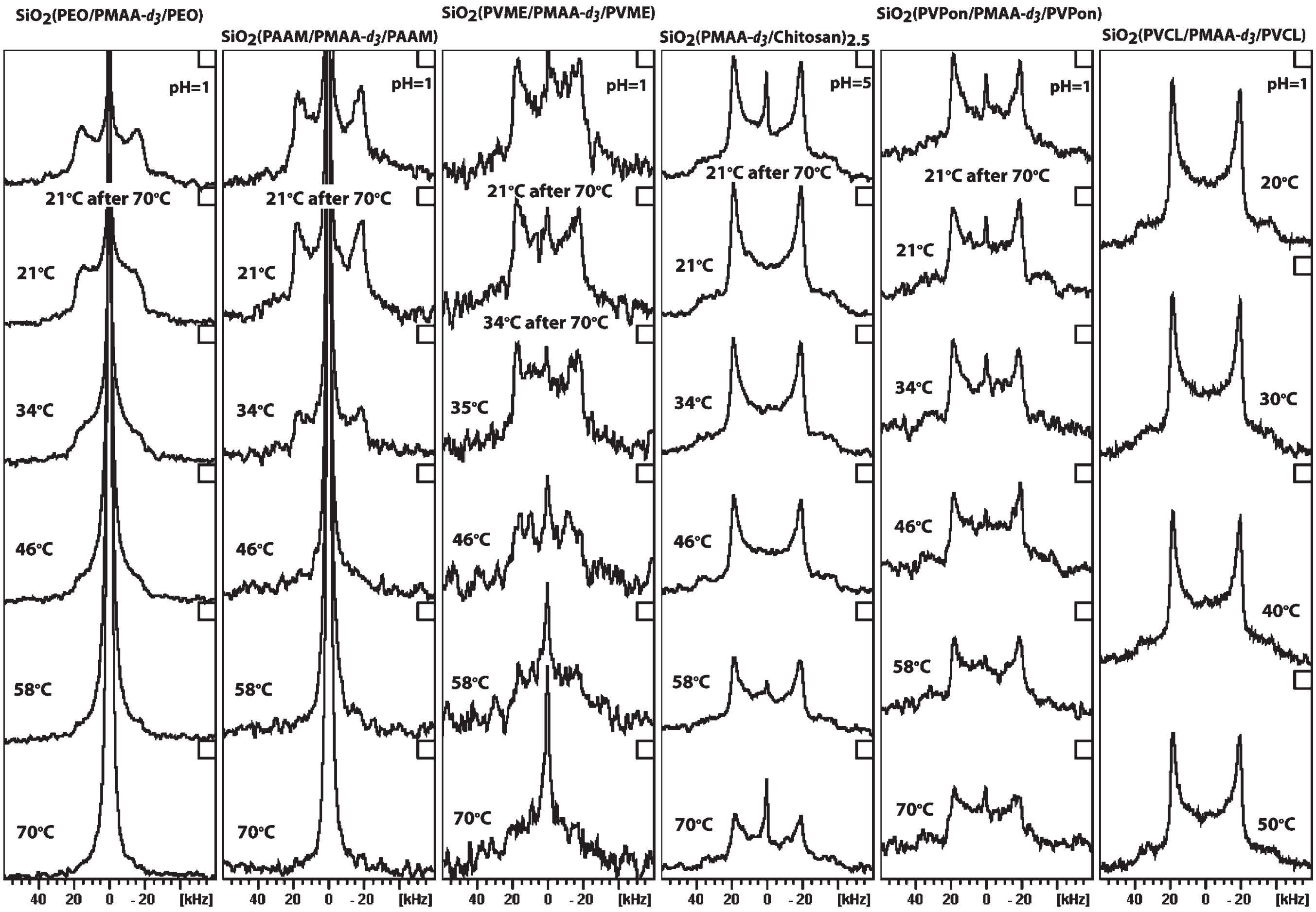


**Figure 6.** Variable temperature $^2$H NMR of PMAA-$d_3$ supported multilayers saturated with pH 1.3 deuterium depleted water with the exception of chitosan that was saturated with pH 5 deuterium depleted water.

complexes and heated. As seen in Figure 4, the hydrated PMAA-$d_3$ spectrum with pH value <2 is dominated by a large broadened isotropic component due to swollen chain segments, but there is a small Pake contribution arising from solidlike restricted motion that collapses with heating. Even in dilute aqueous solutions, PMAA is in a compact, "hypercoiled" state below a pH value of 5, leading to broad lines in the $^1$H and $^{13}$C NMR spectra.[29] Although there is no consensus on the origin of the stability of the compacted form of PMAA, hydrophobic forces, van der Waals, and inter- and intramolecular hydrogen-bonding interactions have been invoked.[30] If, after heating, the hydrated PMAA-$d_3$ is left to equilibrate at room temperature for an extended period, >12 h, the $^2$H NMR spectrum returns to its initial state, suggesting that any rearrangement of the hydrogen bonds incurred is reversible. Within the hydrated complexes, heating likewise results in the onset of PMAA chain mobility with the breaking and rearrangement of the inter- and intrapolymer hydrogen bonds.

While hydrogen bonds usually start to dissociate at higher temperatures, the hydrophobic interactions simultaneously increase in strength. Electron-donating groups connected through a backbone carbon to the carboxylic acid group, such as methyl or ethyl, are predicted to increase the hydrogen bond energy and simultaneously decrease the acidity.[31] Therefore, the hydrogen bond energies of PMAA complexes are larger than those of PAA. In addition to the hydrogen bond energy, the fraction of carboxylic acid groups participating in hydrogen bonds contributes to the overall strength of complexation. The fraction of H-bonded carboxylic groups in multilayer films was measured to be ∼0.5 in PVPon/PMAA but only ∼0.1 in the PEO/PMAA.[15] The trend in the onset of chain mobility with heating, summarized in Table 3, mirrors the PMAA complexation strength due to the number of H-bond linkages and increasing hydrophobic forces in the series PEO < PAAM < PVME < PVPon < PVCL.

The $^2$H NMR spectra of the PMAA complexes were all taken at pH value of 1.3, far below the critical pH values for the multilayer films of these complexes. The critical pH value for the PEO/PMAA multilayers is 4.6. When the solution of the aqueous suspension of the bulk complex is raised to a pH value of 5.0, there is a large isotropic peak at lower temperatures as expected for partial dissolution (Figure 5). The variable temperature $^2$H NMR spectra show that the remaining broad component at a pH value of 5 collapses in the same temperature range as the complex below its critical pH value, indicating that the remaining complexed portions have the same phase behavior. It has been shown that, upon raising the solution pH value, PVPon/PMAA capsules do not swell but rather the wall thickness decreases along with an increase in surface roughness attributed to microphase separation of the component polymers.[24] This process occurs at a much lower pH value in the case PEO/PMAA due to weaker hydrogen bonds. Here, the hydrogen bonding strength has been defined by

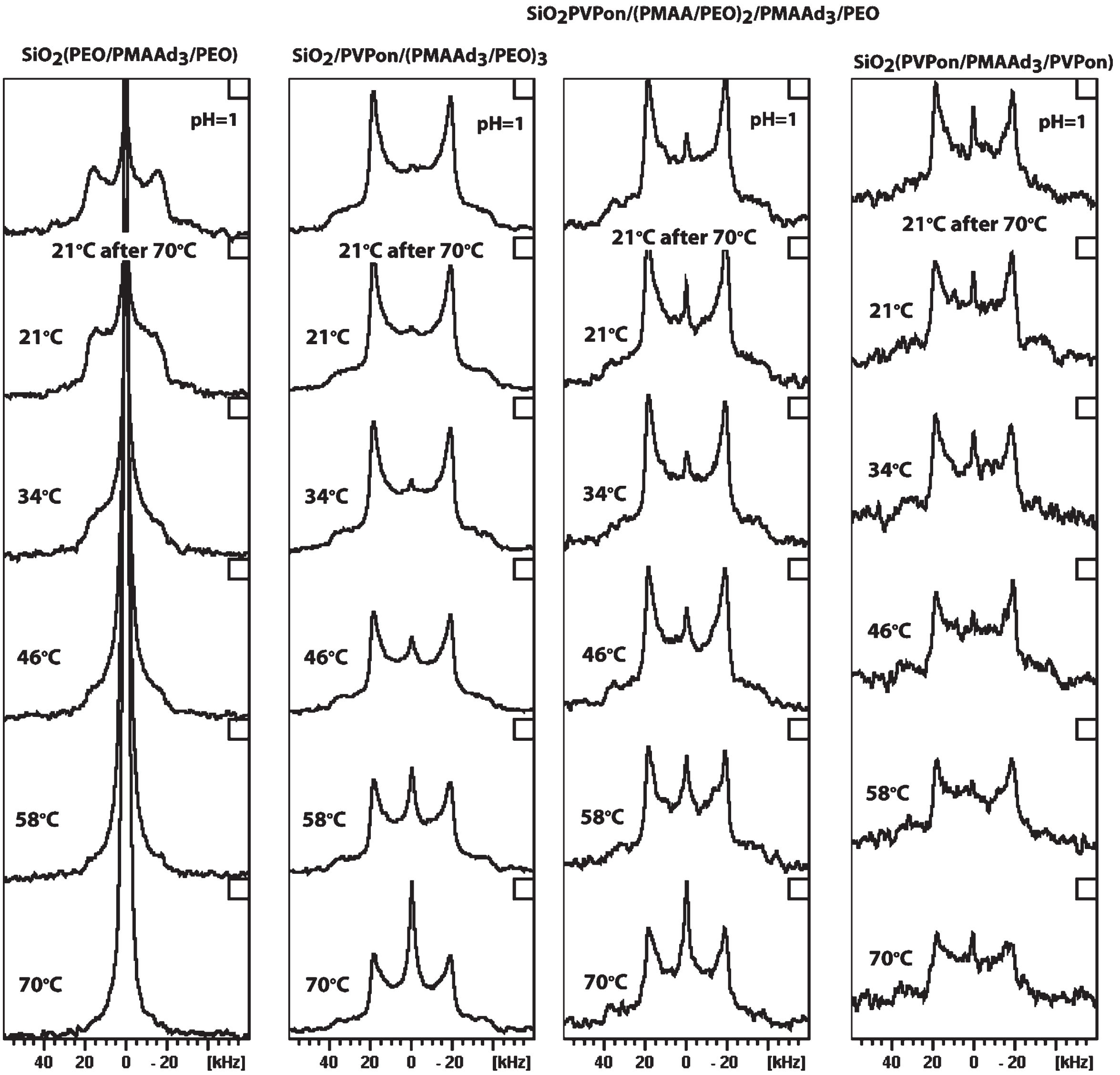


**Figure 7.** $^2$H NMR spectra of (a) (PEO/PMAA-$d_3$/PEO), (b) (PVPon)/(PMAA-$d_3$/PEO)$_3$, (c) (PVPon)/(PMAA/PEO)$_2$/(PMAA-$d_3$/PEO), and (d) (PVPon/PMAA-$d_3$/PVPon) layers deposited on silica colloids and saturated with deuterium depleted water.

Sukhishvili and Granick[15] as the amount of ionization tolerated before disassembly of the multilayers occurs, where stronger hydrogen bonds tolerate a higher amount of ionization. They also suggest that it is hydrogen bonding itself that suppresses the ionization of the carboxylic acid groups of PMAA, rather than the hydrophobic environment.[15]

The $^2$H NMR spectra of the multilayers, deposited by the LBL method onto silica colloids, are presented in Figure 6. Three layers were deposited, starting with the hydrogen-bond acceptor polymer followed by PMAA and the outer layer the hydrogen-bond acceptor polymer. As mentioned previously, PMAA-capped silica colloids and hollow capsules tend to aggregate due to the intrapolymer hydrogen bonding of PMAA. Because of the relatively small amount of material, the signal-to-noise is lower than that of the complexes, and in some samples there is a significant isotropic contribution from DCl/D$_2$O content in the concentrated HCl used to acidify the deuterium depleted water that was used. However, qualitatively, the water-saturated, supported multilayers show the same relative trend in chain mobilities as the aqueous dispersions of the PMAA bulk complexes. The PMAA layered with PVPon or PVCL remains in a glassy state, the chitosan/PMAA multilayers show the onset of intermediate motion upon heating, and significant fast motion (isotropic components) is observed for PMAA layered with PVME, PAAM, and PEO.

As mentioned previously, stable PEO/PMAA hollow capsules could only be prepared by depositing a primer layer of polymer to serve as an anchor as PEO binds too weakly to the silica surface. The effect of this primer layer, which in our case is PVPon, on the chain dynamics of the multilayers is seen in Figure 7, a comparison of the PEO/PMAA multilayers with and without a primer layer to the PVPon/PMAA multilayers. The addition of the single PVPon layer changes the dynamics throughout the three bilayers of PEO/PMAA, restricting the mobility so that a Pake contribution persists to the highest temperature examined, similar to the behavior of the PVPon/PMAA multilayer. A $^2$H NMR spectrum of the multilayer sample where only the last PMAA layer is deuterated proves that the broad component is not just due to complexation of the PVPon primer layer with the first PMAA layer but is associated with the entire multilayer. This observation correlates with several other studies. Neutron diffraction demonstrated that strong H-bonded complexes like PVPon/PMAA form more stratified multilayers but with interlayer roughnesses of ∼3.5 nm still interpenetrate over several bilayers, as compared to weak H-bonded PEO−PMAA films that are completely interdiffused.[3]

The restricted mobility of the PEO−PMAA multilayers prepared with a PVPon primer layer is a manifestation of this interdiffusion of the layers. The extent of interlayer mixing as probed by the PMAA chain mobility is also relevant to recently reported free-standing films that are produced by first depositing multilayers of PMAA with a thermoresponsive polymer (PNIPAM) followed by PMAA−PVPon multilayers.[17] The critical pH value of films containing thermoresponsive polymers depends on temperature and, in the case of polymers with a LCST, decreases as the temperature is lowered. The top PMAA layers complexed with the nonthermoresponsive PVPon are released when the temperature is lowered since the critical pH value of the bottom thermoresponsive layers falls below the solution pH value. If an insufficient number of thermoresponsive bottom layers are deposited, the PMAA−PVPon film is not released because the PVPon interdiffuses enough into the bottom layers to prevent their disintegration. Accordingly, the release time is strongly dependent on the number of thermoresponsive layers, only reaching a steady state value above 10 bilayers.[17] Whereas the effect of interlayer mixing on the temperature triggered release films is due to PVPon diffusing down into the layers next to the substrate, we are observing the extent of the diffusion of the first surface anchored PVPon layer into the upper layers.

Since primer layers are commonly used to adhere multilayers to surfaces, our results show that the effect of these layers on the film dynamic properties must be considered. A study of the role of PEI primer layers in stabilizing weakly H-bonded multilayers on particulate substrates concluded that the unfavorable flat conformation formed by PEI deposited at low pH values inhibited the film growth.[23] Depositing the PEI primer layer at a higher pH value where it takes on a more loopy conformation, followed by multilayer deposition at a low pH value stabilized the PEO/PMAA films. However, hollow capsules of weakly hydrogen-bonded complexes could not be produced unless one bilayer of PMAA/PVPon was deposited after the PEI primer, followed by three PEO/PMAA bilayers. We found that using a PVPon primer layer was sufficient for producing hollow PEO/PMAA capsules from silica colloids (Figure 1). The $^2$H NMR results for the three PMAA/PEO bilayers with the PVPon primer layer indicate this stabilization is due to the extensive interdiffusion of the PVPon.

## 4. CONCLUSIONS

Wide-line solid-state $^2$H NMR has been applied to quantify the molecular level dynamics of PMAA within a series of complexes and supported multilayers that are saturated with acidic deuterium depleted water. The low-$T_g$, intrinsically mobile polymers, PEO and PVME, form relatively weak and mobile PMAA complexes. PMAA also displays enhanced chain mobility when complexed to PAAM, a high-$T_g$ polymer when dry due to strong hydrogen bonding. In this case, PAAM's thermoresponsive behavior (UCST at 25 °C when complexed to PAA), in addition to the lack of hydrophobic stabilization, determines the PMAA dynamics. However the thermoresponsive properties of PVME and PVCL had little to no effect on the PMAA chain dynamics as expected since complexes of polymers with LCSTs are known to stabilize with heating. We therefore conclude that the hydrophobic character of the partner polymer in a PMAA complex or multilayer stabilized by hydrogen bonds primarily determines the chain mobility. Through the selection of appropriate partner polymers, the chain mobility and related properties of PMAA-based multilayers can be continuously tuned, ranging from highly mobile for hydrophilic polymers (PEO or PAAM) where fast isotropic motion is observed to dominate, to a thermally stable glassy state for partner polymers with significant hydrophobic character (PVPon or PVCL). This trend in the chain level dynamics correlates well with the properties of hydrogen-bonded polymer multilayers in contact with water, specifically the layer thickness, permeability, and critical pH value. Finally, the effect of a primer layer, commonly used to adhere weakly complexed polymer multilayers to solid surfaces, on the chain dynamics confirms the extent of interpenetration for H-bonded polymer multilayers.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Details regarding the synthesis and characterization of the labeled PMAA-$d_3$; SEM images and notes regarding the effects of long-term storage of multilayer polymer capsules in HF; Figures demonstrating the LBL growth of the PVPon primed PEO multilayers; details of how the deuterium line shape is affected by orientation and motion and the fits of a series of spectra acquired with different echo delay times to assist the validation of the 30-site diffusion type simulation model used. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: linda.reven@mcgill.ca.

## ■ ACKNOWLEDGMENT

We acknowledge the assistance of Dr. Cedric Malveau (U. Montreal) with NMR spectroscopy, Line Mongeon with SEM, Dr. Roumen Christov with mass spectroscopy, and Petr Fiurasek for training on the triple detection GPC and the TGA. Funding for this research was provided by Fonds québécois de la recherche sur la nature et les technologies (FQRNT) and the Natural Sciences and Engineering Research Council of Canada (NSERC).

## ■ REFERENCES

(1) Kharlampieva, E.; Sukhishvili, S. A. *Polym. Rev.* **2006**, *46*, 377–395.

(2) Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv. Polym. Sci.* **1999**, *46*, 121–196.

(3) Kharlampieva, E.; Kozlovskaya, V.; Ankner, J. F.; Sukhishvili, S. A. *Langmuir* **2008**, *24*, 11346–11349.

(4) Schlenoff, J. B. *Langmuir* **2009**, *25*, 14007–14010.

(5) (a) Smith, R. N.; Reven, L.; Barrett, C. J. *Macromolecules* **2003**, *36*, 1876. (b) McCormick, M.; Smith, R. N.; Graf, R.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Macromolecules* **2003**, *36*, 3616–3625. (c) Smith, R. N.; McCormick, M.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Macromolecules* **2004**, *37*, 4830–4838.

(6) Fortier-McGill, B.; Reven, L. *Macromolecules* **2009**, *42*, 247–254.

(7) Sukhishvili, S. A.; Kharlampieva, E.; Izumrudov, V. *Macromolecules* **2006**, *39*, 8873–8880.

(8) Aldrich Polymer Products Application & Reference information.

(9) Hancock, B. C.; Zografi, G. *Pharm. Res.* **1994**, *11*, 471–477.

(10) Meeusen, F.; Nies, E.; Berghmans, H.; Verbrugghe, S.; Goethals, E.; Du Prez, F. *Polymer* **2000**, *41*, 8597–8602.

(11) Sakurai, K.; Maegawa, T.; Takahashi, T. *Polymer* **2000**, *41*, 7051–7056.

(12) Yanul, N.; Kirsh, Y.; Anufrieva, E. *J. Therm. Anal. Calorim.* **2000**, *62*, 7–14.

(13) Maeda, Y. *Langmuir* **2001**, *17*, 1737–1742.

(14) Chu, L. Y.; Li, Y.; Zhu, J. H.; Chen, W. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2124.

(15) Sukhishvili, S.; Granick, S. *Macromolecules* **2002**, *35*, 301–310.

(16) Kharlampieva, E.; Kozlovskaya, V.; Tyutina, J.; Sukhishvili, S. A. *Macromolecules* **2005**, *38*, 10523–10531.

(17) Zhuk, A.; Pavlukhina, S.; Sukhishvili, S. A. *Langmuir* **2009**, *25*, 14025–14029.

(18) Khutoryanskiy, V. V.; Nurkeeva, Z. S.; Mun, G. A.; Dubolazov, A. V. *J. Appl. Polym. Sci.* **2004**, *93*, 1946–1950.

(19) Kotov, N. A. *Nanostruct. Mater.* **1999**, *12*, 789–796.

(20) Ayrey, G.; Wong, D. J. D. *J. Labelled Compd. Radiopharm.* **1978**, *14*, 935–944.

(21) Beckmann, P. A.; Dybowski, C. *J. Magn. Reson.* **2000**, *146*, 379–380.

(22) Witterbort, R. J.; Olejniczak, E. T.; Griffin, R. G. *J. Chem. Phys.* **1987**, *86*, 5411.

(23) Kozlovskaya, V.; Yakovlev, S.; Libera, M.; Sukhishvili., S. A. *Macromolecules* **2005**, *38*, 4828–4836.

(24) Elsner, N.; Kozlovskaya, V.; Sukhishvili, S. A.; Fery, A. *Soft Matter* **2006**, *2*, 966–972.

(25) Metin, B.; Blum, F. D. *J. Chem. Phys.* **2006**, *124*, 054908.

(26) Chen, S.; Lui, M.; Jin, S.; Chen, Y. *J. Appl. Polym. Sci.* **2005**, *98*, 1720–1726.

(27) Metin, B.; Blum, F. D. *J. Phys. Chem.* **2006**, *125*, 054707.

(28) (a) Miyoshi, T.; Takegoshi, K.; Terao, T. *Macromolecules* **1999**, *32*, 8914–8917. (b) Myoshi, T.; Takegoshi, K.; Hikichi, K. *Macromolecules* **1996**, *37*, 11–18.

(29) Sugai, S.; Nitta, K.; Toyama, Y. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 47–51.

(30) Ruiz-Perez, L.; Pryke, A.; Sommer, M.; Battaglia, G.; Soutar, I.; Swanson, L.; Geoghegan, M. *Macromolecules* **2008**, *41*, 2203–2211.

(31) (a) Tao, L.; Han, J.; Tao, F.-M. *J. Phys. Chem. A* **2008**, *112*, 775–782. (b) Peljhan, S.; Zagar, E.; Cerkovnik, J.; Kogej, K. *J. Phys. Chem. B* **2009**, *113*, 2300–2309.