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Simple and facile synthesis of water-soluble poly(phosphazenium) polymer electrolytes

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Abstract

Water-soluble polymer electrolytes are important industrial materials used as absorbents, rheology modifiers, network formers, and colloidal stabilizers and destabilizers. Herein, the synthesis and alkaline stability of a new class of water-soluble polymer poly(phosphazenium) electrolytes is reported. The charge on the poly(phosphazenium) structure was controlled by the amount of methylating agent used and the resultant electrolytes were water-soluble with a relative small amount of charge per polymer chain (one charged group per 10 repeat units). Despite phosphazenium salts having excellent alkaline stability, the poly(phosphazenium) polymers with N-methylcyclohexyamino substituents degraded rapidly in alkaline solutions at 60 °C. Two-dimensional NMR was used to characterize the poly(phosphazenium) polymer electrolytes and their hydroxide ion induced degradation products.

Introduction

Polymer electrolytes have a wide range of aqueous applications that include absorption, osmotic control, rheology modification, complexation or network formation, catalysis, and colloid or emulsion stability.[1] They play a pivotal role in several types of industrial processes and consumer products that span pharmaceutical and drug delivery products, oil recovery, thickening of paints and adhesives, membrane and chromatographic separations, solids recovery in mining, water clarification, complex coacervates, phase transfer catalysts, antimicrobial reagents, flocculants, and separators in electrochemical devices like fuel cells, batteries, and electrodialysis cells.[1-3]

A significant challenge in polycation polymer electrolytes (which includes anion exchange polymer electrolyte membranes (AEMs)) is the alkaline stability of the tethered cation and polymer backbone in the presence of hydroxide ions – which are potent nucleophiles. Degradation of cation groups via hydroxide ion attack has several severe consequences that include reduced AEM ion conductivity and loss of water solubility and absorbance by the polycation.

A recent resurgence of interest in AEM-based alkaline fuel cells (AEMAFCs) and water electrolyzers (AEMWEs) has reiterated the fundamental challenges associated with making alkaline stable AEMs and polycations.[4-9] AEMAFCs and AEMAWEs are attractive candidates for replacing current acidic proton exchange membrane fuel cells and water electrolyzers because the alkaline environment enables the use of non-platinum group metals for catalyzing the oxygen reduction/evolution reaction. Although AEM stability in 1 M KOH up to 40 days at 80 °C has been established[10-14], long-term alkaline stability over 40 days (a new U.S. DOE established target – 1000 hours ~ 42 days)[15] has yet to be achieved.

AEM degradation can take place at the affixed cationic group or on the fixed polymer backbone chain. It is recognized that poly(aryl ether) backbones with cations at the benzyl position suffer from polymer backbone degradation in alkaline media.[16, 17] Alternative backbones, like polystyrene copolymers, polyethylene, polyphenylene, and radiation grafted ethylene tetrafluoroethylene, are reported to be more resilient in alkaline solutions.[10, 13, 18, 19] Poly(aryl ether)s can be rendered more stable via alteration to their morphology[11] or by using spacer pendants that separate the cation further away from the backbone[20]. The cation groups in AEMs can also degrade through multiple mechanisms including Hoffman elimination, direct nucleophilic substitution (e.g., debenzylation, dearlyation, dealkylation), ring-opening, and ylide-intermediates that foster rearrangement reactions.[7, 21, 22] Many researchers have investigated alternative cation chemistries, tethering strategies, and more recently, alteration to membrane morphology to improve cation stability.[11, 12, 14, 23]

Phosphazeniums are a class of cation salts documented to have excellent alkaline stability.[24] Schwesinger and co-workers prepared several generations of phosphazenium cations (i.e., branched phosphazeniums).[25-27] The generation 1 (i.e., no branching) phosphazenium cation with N-methylcyclohexylamino substituents demonstrated superior alkaline stability at 100 °C in 50 wt% NaOH in chlorobenzene.[24] Increasing the size of the phosphazenium group via branching to a generation 4 type yielded even better alkaline stability under the same test conditions. Noonan *et al.* attached N-methylcyclohexylamino substituted phosphazenium cations to a polyethylene backbone and their AEM demonstrated remarkable alkaline stability in 1 M KOH at 80 °C for 22 days.[10] However, phosphazene bases with N-methylcyclohexylamino substituents are not commercially available.

In this work, we set out to develop a new class of AEMs from commercially available polydichlorophosphazene (PDCP) polymers. In our synthesis, the chloro groups in PDCP were substituted with N-methylcyclohexylamino groups via an amination reaction – a well-documented scheme for the preparation of aminated poly(phosphazenes).[28] The charged polymer, poly(phosphazenium), was created by methylating the nitrogen in the polymer backbone using dimethylsulfate (DMS). To our surprise, adding alkylating agent to the poly(N-methylcyclohexylamino phosphazene) (PMCHAP) yielded water-soluble poly(N-methylcyclohexylamino phosphazenium) ($PMCHAP^+$) polymers even when just 1 out of 10 repeating units was functionalized to the cation form. This result challenged our perception of the structure formed upon alkylation causing us to rethink the structure formed. The water-soluble $PMCHAP^+$ polymer was dissolved in deuterated aqueous alkaline solutions (1 M NaOD in D_2O) and stored at 60 °C for 3 days. NMR spectra of the $PMCHAP^+$ exposed to alkali revealed significant degradation. This is the first report, to the best of our knowledge, describing the preparation and evaluation of poly(phosphazenium) polyelectrolytes.

Experimental

Preparation of poly(N-methylcyclohexylamino phosphazene) (PMCHAP) - The precursor polydichlorophosphazene (PDCP) (MW ~ 150,000 g/mol received from CM-Tec, Inc.) was weighed out in a glove box under argon. The polymer was added to a round-bottom flask. Note: All glassware used in the glove box was dried at 130 °C for 12 hours to remove residual moisture. Anhydrous N,N-dimethylacetamide (DMAc) was used to dissolve the polymer to prepare a 5 wt% solution (e.g, 5 g PDCP into 101 mL of DMAc). A 3:1 ratio of N-methylcyclohexylamine (stored under molecular sieves to remove residual moisture) per chlorine atom in the PDCP was added to the solution (e.g., to the 5 g PDCP batch in 101 mL of DMAc – approximately 30 g of N-methylcyclohexylamine was added). An egg-shaped stir-bar was added to the flask and the flask was sealed and removed from the glove box. The solution was stirred and heated to 80 °C for 16 hours. The resultant solution was precipitated in methanol. The solid obtained was dissolved in chloroform, precipitated in methanol, collected by vacuum filtration, and vacuum dried at 60 °C for 12 hours. Nearly 100% recovery of the polymer was achieved.

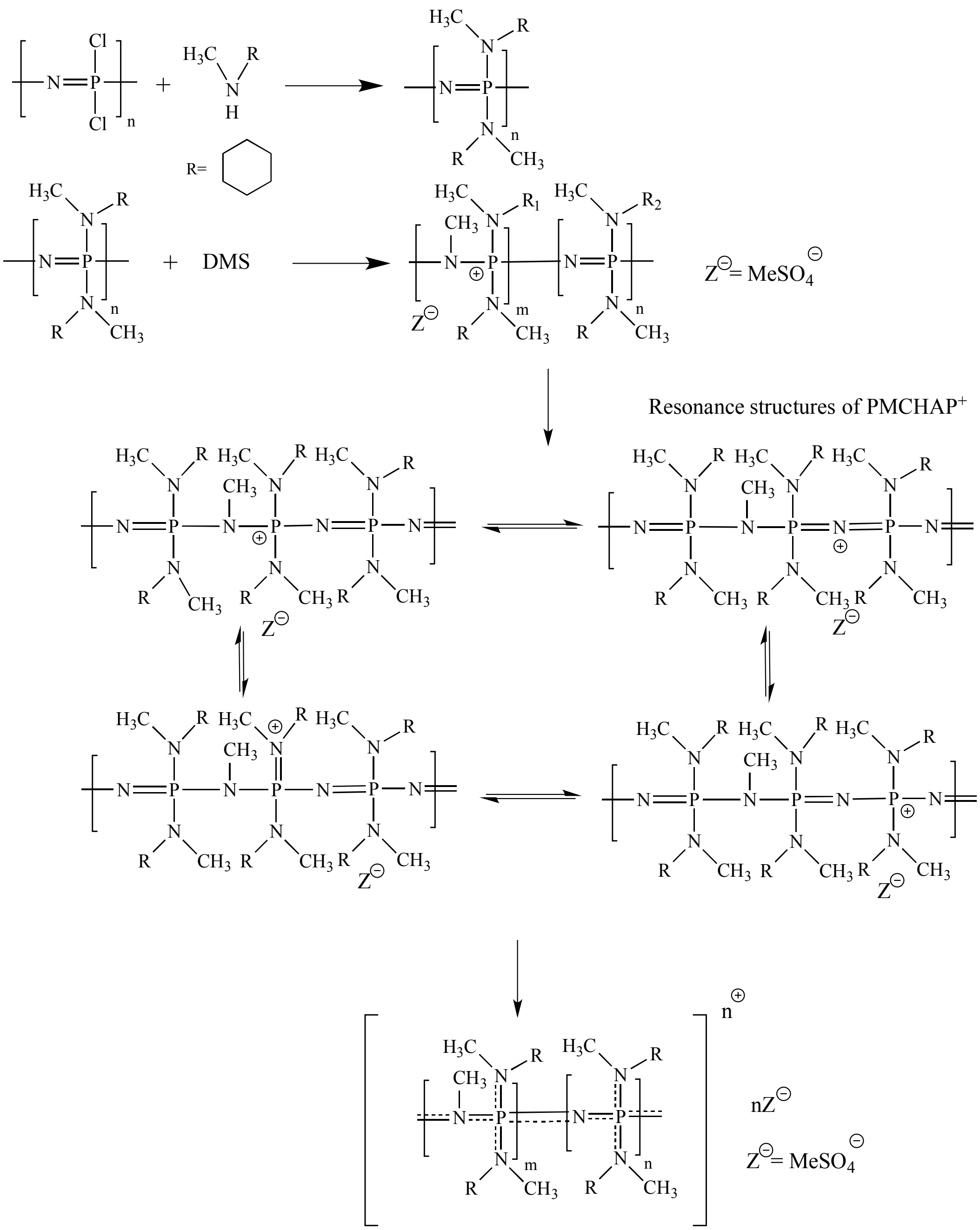
Preparation of poly(N-methylcyclohexylamino -phosphazenium) (PMCHAP$^+$) - PMCHAP solid was dissolved in anhydrous NMP (e.g., 5 wt% - 10 g PMCHAP into 184 mL of NMP). The solution was heated to 80 °C while stirring. DMS was added as the limiting reagent to control the degree of methylation to PMCHAP$^+$. The 'Results and Discussion' section detail the amount of DMS added to the different batches prepared. The flask was sealed and the reaction was allowed to proceed for 24 hours. The resultant solution was poured into a petri dish. The solvent was evaporated at 80 °C for 12 hours.

A film was obtained, but broke apart during removal from the petri dish. The collected solid was observed to dissolve in deionized water. Approximately100% of the polymer was recovered.

Alkaline stability tests - 400 mg of PMCHAP$^+$ was placed in a 30 mL polypropylene container and dissolved with 10 mL of 1 M NaOD in D_2O. After the samples were exposed to the alkaline solution for 3 days at 60 °C, 600 μL of sample was removed from the polypropylene container and transferred to an NMR tube. The NMR spectra collected for each sample were 1D ^{1}H NMR, ^{1}H NMR (phosphorus decoupled), ^{13}C NMR (proton decoupled), and 2D homonuclear correlation spectroscopy (COSY), ^{1}H-^{13}C heteronuclear multiple quantum correlation spectroscopy (^{1}H-^{13}C HMQC), and ^{1}H-^{31}P heteronuclear multiple quantum correlation spectroscopy (^{1}H-^{31}P HMQC) spectroscopy. Procedures for NMR experiments have been described in our previous papers[17, 22] and the details describing them are included in the electronic supplementary information (ESI) section under Table S1.

Results and Discussion

Scheme 1 illustrates the method used to prepare PMCHAP$^+$. PDCP was reacted with an excess amount of N-methylcyclohexylamine to produce PMCHAP. The collected product was then reacted with DMS to create phosphazenium groups and yield PMCHAP$^+$. Figure 1 provides the ^{31}P NMR spectra of PDCP, PMCHAP, and PMCHAP$^+$. The two observed peaks in the PDCP trace (see Figure 1a) corresponded to i.) the phosphorus in the PDCP repeat units bonded with two chloro groups (chemical shift (δ) = -17 ppm)[26] and ii.) the phosphorus atom in some PDCP repeat units where a chloro group was converted to a phosphorus oxide group due to exposure to residual moisture (δ = 1 ppm). The residual moisture displaces the chloro group with a hydroxyl group that can subsequently convert to the more stable tautomer phosphorus oxide compound.[29] Note: residual moisture could have leaked into the NMR tubes sealed with a plastic cap upon its removal from the glove box or residual moisture could have been present in the deuterated chloroform solution. The phosphorus group in PMCHAP had a broad peak ranging from δ = -10 ppm to -14 ppm. See Figure 1b. The PMCHAP sample did not display any peaks corresponding to phosphorus oxide in the ^{31}P NMR spectra confirming that hydrolysis of the precursor did not take place during the reaction and the initial premise that the hydrolyzed PDCP observed in Figure 1a was due to moisture leaking into the NMR tube or residual moisture being present in the deuterated chloroform. Reacting PMCHAP with DMS resulted in two new peaks at δ = -9 ppm and 1 ppm in the ^{31}P NMR spectrum of PMCHAP$^+$. The creation of the two new peaks offered evidence that phosphazenium groups (i.e., alkylamino phosphonium cations) were created in the polymer backbone chain. See Figure 1c. This is the first report, to the best of our knowledge, of the methylation of aminated poly(phosphazene) to water-soluble poly(phosphazenium) polymer electrolytes.



Scheme 1. Synthesis scheme describing $PMCHAP^+$ synthesis and $PMCHAP^+$ resonance structures

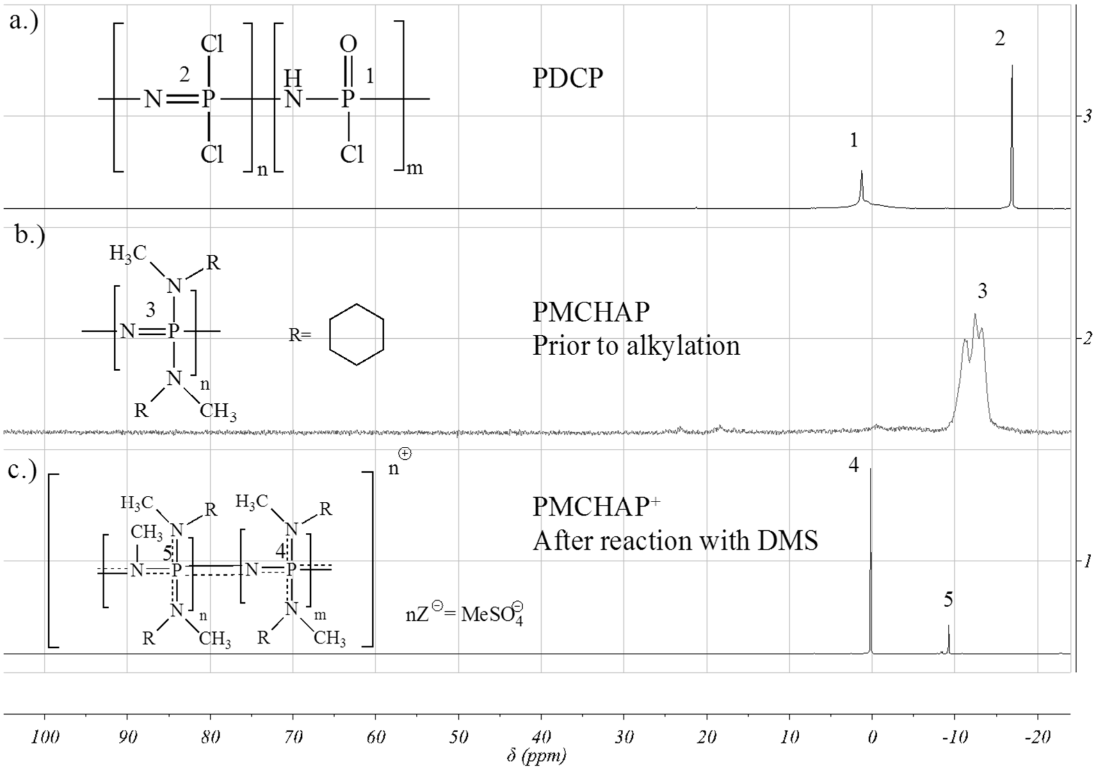


Figure 1. ^{31}P NMR spectra of a.) PDCP, b.) PMCHAP and c.) PMCHAP^{+}. a.) and b.) used $CDCl_3$ as the d-solvent, while c.) used D_2O.

Figures 2a and 2b give the ^{1}H-^{31}P HMQC spectra of PMCHAP and PMCHAP^{+}. In Figure 2a, the '-CH_3' in the attached N-methylcyclohexylamino to the phosphazene backbone demonstrated a heteronuclear coupling at δ = 2.60 ppm for ^{1}H and δ = -10 to -14 ppm for ^{31}P. Reacting PMCHAP with DMS introduced a new peak at 2.64 ppm in the ^{1}H NMR spectrum. This signal corresponded to the protons in two different methyl moieties in the methylated PMCHAP^{+} repeat unit: i.) the methyl group in the N-methylcyclohexylamino substituent and ii.) the methyl group attached to the PMCHAP^{+} linear backbone. The ^{1}H NMR peak at 2.64 ppm showed heteronuclear coupling to the phosphorus peak at δ = -9 ppm. The '-CH_3' group in the PMCHAP demonstrated a ^{1}H-^{31}P coupling at δ = 2.60 ppm for ^{1}H and δ = -10 to 14 for ^{31}P. However, this same '-CH_3'

group in PMCHAP$^+$ demonstrated a different ^{31}P chemical shift at δ = 1 ppm while coupling to the same ^{1}H chemical shift (δ = 2.60 ppm) in PMCHAP$^+$'s ^{1}H-^{31}P HMQC spectrum. This '-CH_3' coupling in PMCHAP$^+$'s ^{1}H-^{31}P HMQC spectrum at δ = 2.60 ppm for ^{1}H and δ = 1 ppm for ^{31}P was assigned to the non-methylated repeat units in PMCHAP$^+$. See Figure 2b. The downshifting in the phosphorus chemical shift of the '-CH_3' coupling from δ = -10 to -14 ppm in PMCHAP to δ =1 ppm in PMCHAP$^+$ revealed that the non-methylated repeat units' phosphorus atom in PMCHAP$^+$ had more electron withdrawing character. This could only arise from charge delocalization created by resonance. Hence, methylating a repeat unit resulted in the non-methylated repeat units obtaining a positive charge.

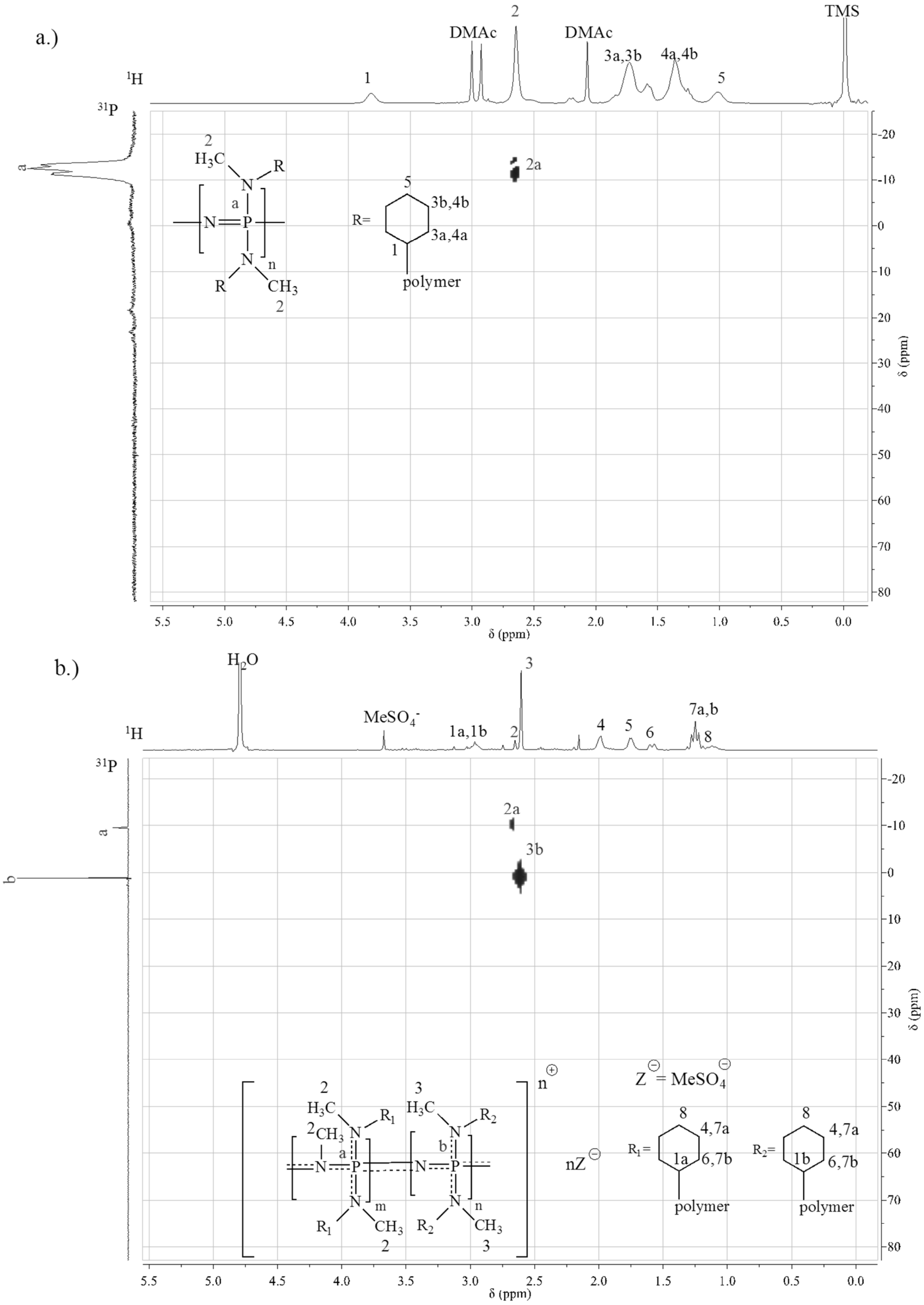


Figure 2. ^{1}H-^{31}P HMQC spectra of a.) PMCHAP and b.) PMCHAP^{+}. a.) used d-DMAc as the NMR solvent while b.) used D_2O as the NMR solvent.

Figures 1c and 2b represent the PMCHAP$^+$ batch where 0.25 moles of DMS per phosphazene repeat unit were added. This was PMCHAP$^+$ batch #1. When we obtained this initial PMCHAP$^+$ batch and observed its water solubility, we postulated that the ionic content was too high in batch #1 leading to the water-soluble polymer. Therefore, we reduced the amount of DMS to 0.1 mol per repeat unit when preparing batch #2. However, batch #2 of PMCHAP$^+$ was also water-soluble. This unexpected water solubility was attributed to the fact that methylation of a repeat unit resulted in a distributed positive charge along the polymer chain due to resonance effects.

Table S2 in the ESI section provides the average degree of methylation per repeat unit as determined by integrating the ^{1}H and ^{31}P NMR spectra of PMCHAP$^+$. Integrating the ^{31}P NMR spectra at $\delta = -9$ ppm and $\delta = 1$ ppm for PMCHAP$^+$ demonstrated that most of the DMS added to the batch reacted with PMCHAP. Similarly, integrating the peaks in the ^{1}H NMR at $\delta = 2.60$ ppm and at $\delta = 2.64$ ppm agreed closely with the ^{31}P NMR integration results. Figures S1a and S1b in the SI section provide the integrated ^{1}H NMR and ^{31}P NMR of PMCHAP$^+$ spectra along with the calculations. The counterion produced after methylation was methyl sulfate ($MeSO_4^-$) and integrating this peak in Figure S1a at $\delta = 3.68$ ppm matched the integration value of the methyl group added to the poly(phosphazene) backbone during the methylation reaction to produce PMCHAP$^+$. In other words, the matching integration values at $\delta = 3.68$ ppm and $\delta = 2.64$ ppm demonstrated that the total positive charge of the PMCHAP$^+$ equaled the amount of counteranions in the system. This result also substantiated the reaction scheme to produce poly(phosphazenium) polymer electrolytes. An interesting feature of this polymer was that the non-methylated repeat units were still amenable to methylation even though they carried a distributed positive charge because of resonance. In the non-methylated repeat units, the phosphorus atom can carry the positive charge making the adjacent nitrogen atom on the linear backbone susceptible to methylation. Increasing the degree of methylation of the polymer chain resulted in an increased positive charge on the polymer backbone. Figure S2 in the ESI section illustrates a PMCHAP$^+$ chain with 4 out of 10 repeat units methylated with different resonance structures. In summary, both Figure 2a and 2b confirmed that the amination reaction and subsequent alkylation reaction were successful. Figures S3 to S4 in the ESI section provide the corresponding COSY and ^{1}H-^{13}C HMQC spectra of PMCHAP and PMCHAP$^+$. These spectra also confirmed attachment of the N-methylcyclohexylamino group to the polymer backbone and of the methyl group upon methylation. In particular, the COSY spectra in Figures S3a and S3b helped identify the signals from the cyclohexyl ring because these protons in the ring displayed J-coupling resulting in 'off-diagonal' signals observed in the COSY spectra.

To evaluate alkaline stability, PMCHAP$^+$ was dissolved in 1 M NaOD in D_2O and stored at 60 °C for 3 days. Figure 3 shows the ^{1}H-^{31}P HMQC spectrum of the alkaline exposed PMCHAP$^+$, while Figure 4 outlines the primary degradation mechanisms deduced. From Figure 3, only one of the three peaks observed in the ^{31}P NMR trace displayed heteronuclear coupling to protons. This coupling, observed at 3.3 ppm for ^{1}H NMR and 6 ppm for ^{31}P NMR corresponded to a methyl group coupling to a phosphorus oxide substituent. Two of the other peaks at -4 ppm and 3 ppm in the ^{31}P NMR trace showed no heteronuclear couplings, suggesting that these peaks corresponded to phosphate moieties (e.g., PO_4^{3-}, $NaPO_4^{2-}$, $Na_2PO_4^-$). All three peaks in the ^{31}P NMR trace (at 6 ppm and -4 ppm) were within the expected chemical shift for phosphorus oxide compounds.[30] Figure S5 in the SI section is the COSY spectrum of the $PMCHAP^+$ exposed to alkali and this spectrum helped identify the peaks in the cyclohexyl ring. The amine in the cleaved $PMCHAP^+$ chain (see Figure 4) from hydroxide ion attack would exhibit its proton signals within the chemical shift range of 0.5 to 3.0 ppm. However, the proton signals associated with the cyclohexyl ring in alkaline exposed $PMCHAP^+$ also appeared within the chemical shift range of 0.5 to 3.0 ppm. It was difficult to discriminate between the proton(s) in the amine versus the protons in the cyclohexyl ring. After exposure to the heated alkaline solution, there was some solid precipitate observed at the bottom of the polypropylene container containing the dissolved poly(phosphazenium solution). However, dissolved polymer was certainly present in the liquid phase because the solution still exhibited a yellow color identical to $PMCHAP^+$ dissolved in water. The solid precipitate was not soluble in deuterated solvents like $CDCl_3$ and deuterated dimethyl sulfoxide and N,N-dimethylformamide. Analysis of the solid precipitate will be discussed in a future publication in conjunction with efforts to mitigate the alkaline degradation of poly(phosphazenium) polymer electrolytes. The ^1H-^{13}C HMQC spectrum of $PMCHAP^+$ exposed to alkali could not be obtained because the concentration of the polymer in the liquid phase was low due to the precipitation of the degraded polymer.

Schwesinger and co-workers presented several different degradation modes for phosphazenium salts.[24] In one of the proposed degradation mechanisms, the hydroxide ion can initiate nucleophilic attack on the phosphazenium salt to yield phosphorus oxide. If we consider this mechanism for the alkaline degradation of $PMCHAP^+$, the nucleophilic attack could cleave the polymer chain or remove one of the n-methylcyclohexyamino substituents from the backbone. See Figure 4. We were surprised to observe phosphate in the ^{31}P NMR spectrum because this would indicate that the phosphazene repeat units were continuously attacked by the hydroxide ion to eventually oxidize the phosphazenium repeat unit completely to phosphate. In Schwesinger *et al.*'s and Noonan *et al.*'s work, they demonstrated phosphazenium salts or phosphazeium functionalized to hydrocarbon backbones with significantly better resistance in alkaline media than the PMCHAP$^+$ polymer reported herein. It is important to note that Schwesinger *et al.*'s alkaline stability experiments were performed in chlorobenzene and it has already been demonstrated that the dielectric constant of the medium plays a role in the degradation pathway of hydroxide ion attack on cation groups.[31] Nevertheless, Schwesinger *et al.* demonstrated that some phosphazenium salts were more stable than others based on i.) the generation size (e.g., how branched it was), ii.) the symmetry of the branching, and iii.) the substituents attached to the nitrogen in the phosphazenium salts. Most interestingly, the linearly branched (i.e., asymmetrically branched) phosphazenium salt generation size 2 had relatively poorer stability when compared to tetra n-methylcyclohexylamino phosphazenium salt – which was also used by Noonan *et al.* in his alkaline stable polyethylene anion exchange membranes. One can think of the PMCHAP$^+$ as a long, asymmetrically branched phosphazenium salt that is easily prone to hydroxide ion attack - just like the linearly branched phosphazenium salt generation size 2 reported in Schwesinger *et al.'s* work. Future work will aim to prepare polyphosphazenium polymers with adjacent phosphazene salts in an effort to attain an alkaline stable material. See Figure 5 for an illustrated concept. The side phosphazene groups along the linear polymer chain should provide more steric hindrance and thus make it more difficult for the hydroxide ion to access the polyphosphazenium moiety for attack.

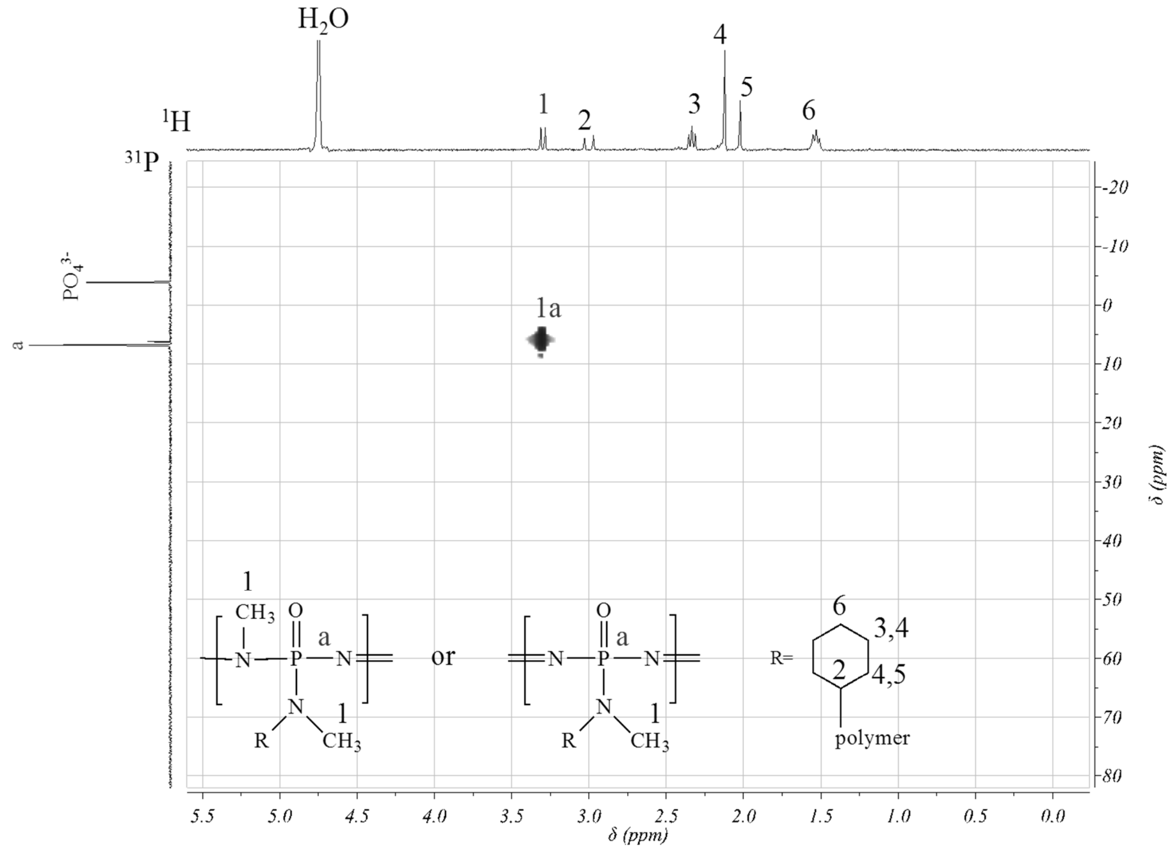


Figure 3. ^{1}H-^{31}P HMQC spectrum of PMCHAP$^+$ after exposure to 1 M NaOD in D_2O for 3 days at 60 °C. NMR solvent for this sample was D_2O.

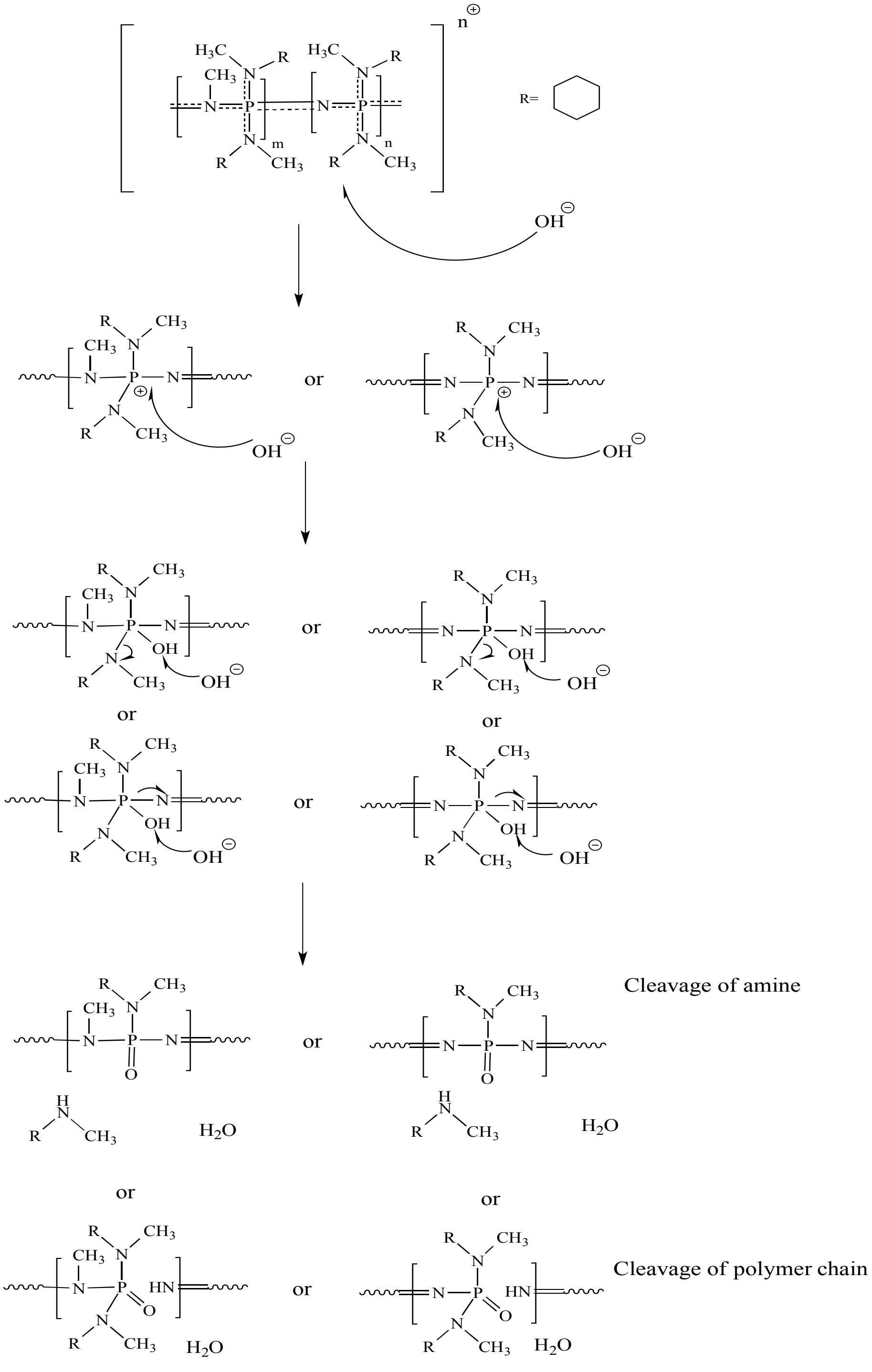


Figure 4. Proposed degradation mechanisms of PMCHAP$^+$ upon exposure to alkaline media.

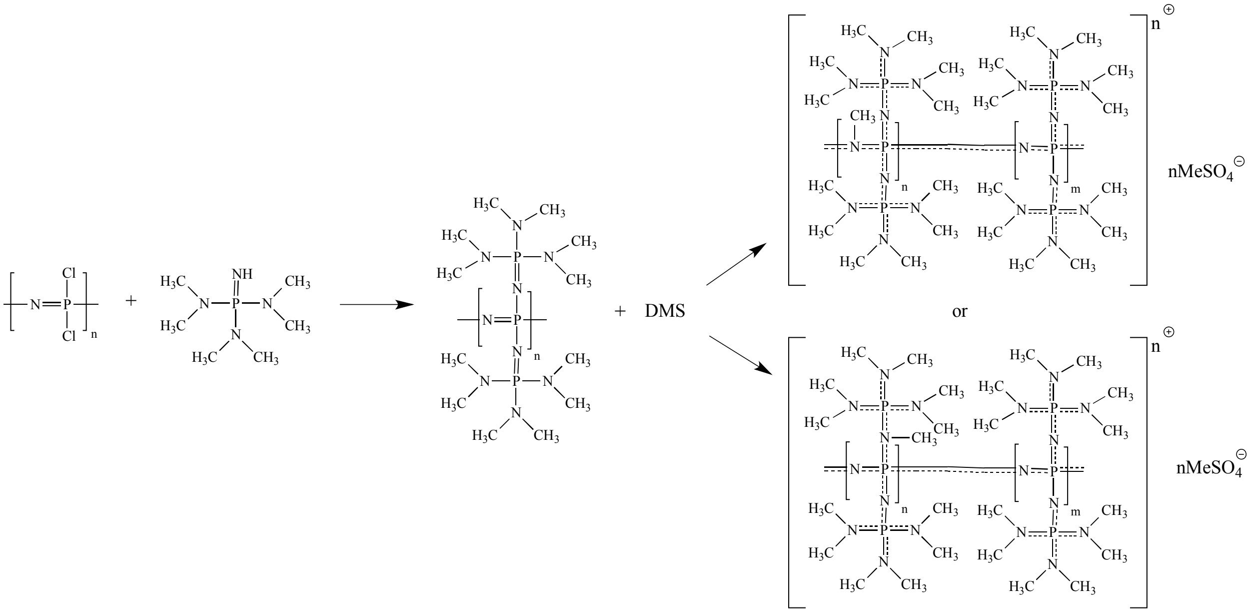


Figure 5. Proposed poly(phosphazenium) polymer for improved alkaline stability.

Conclusion

In conclusion, a simple and facile synthesis of water-soluble poly(phosphazenium) polymers from commercially available PDCP polymers is described. The total positive charge on the polymer chain was controlled via the amount of alkylating reagent added and low total charge per polymer chain (on average – 1 charge per 10 repeat units) still yielded water-soluble polymers. Some variants of phosphazenium salts and AEMs with phosphazenium cations have been shown to have exceptional alkaline stability. However, the PMCHAP$^+$ polymer prepared herein degraded rapidly in alkaline solutions. The poor alkaline stability of the PMCHAP$^+$ was explained by its linear backbone that does not engender sufficient steric hindrance to shield the polymer from hydroxide ion attack. Nevertheless, the water-soluble polymer electrolytes studied herein have many possible applications beyond alkaline applications.

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