Single-Step Application of Polyelectrolyte Complex Films as Oxygen Barrier Coatings

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ABSTRACT: Polyelectrolyte complex (PEC) films such as polyelectrolyte multilayers have demonstrated excellent oxygen barrier properties, but unfortunately, the established layer-by-layer approaches are laborious and difficult to scale up. Here, we demonstrate a novel single-step approach to produce a PEC film, based on the use of a volatile base. Ammonia was used to adjust the pH of poly(acrylic acid) (PAA) so that direct complexation was avoided when it was mixed with polyethylenimine (PEI). Different charge ratios of homogeneous PEI/PAA solutions were successfully prepared and phase diagrams varying the concentration of ammonia or polyelectrolyte were made to study the phase behavior of PEI, PAA, and ammonia in water. Transparent ~1 μm thick films were successfully deposited on biaxially orientated polypropylene (BOPP) sheets using a Meyer rod. After casting the films, the decrease in pH, caused by the evaporation of ammonia, triggered the complexation during drying. The oxygen permeation properties of films with different ratios and single polyelectrolytes were tested. All films displayed excellent oxygen barrier properties, with an oxygen permeation below 4 cm³·m⁻²·day⁻¹·atm⁻¹ (<0.002 barrer) at the optimum ratio of 2:1 PEI/PAA. This ammonia evaporation-induced complexation approach creates a new pathway to prepare PEC films in one simple step while allowing the possibility of recycling.

KEYWORDS: polyelectrolyte complexation, phase diagrams, waterborne coatings, gas barrier, food packaging

1. INTRODUCTION

Thin flexible films with good barrier properties are important for food preservation. Commonly used food packaging materials are laminated multilayers with metal oxides as the gas barrier layer; however, metalized packaging generally lacks transparency, flexibility, and recyclability.¹ To improve these properties, scientists have been focusing mostly on developing polymer matrices with impenetrable nanocomponents, meanwhile balancing the mechanical, optical, and barrier properties. The choices of polymers can be the common synthetic polymers such as polyethylene and polypropylene or bio-based polymers like poly(lactic acid).² The choices of the nanocomponents are more diverse, ranging from metal oxides (TiO₂, ZnO)³,⁴ and two-dimensional (2D) sheets (graphene oxide, layered double hydroxide, and nanoclays)⁵⁻⁷ to bio-based fillers (cellulose nanomaterials).⁸ A recent review has summarized the possible composite materials and their processing routes, where the final reduction in oxygen permeation can vary from as low as 5.6% to almost 100%.⁹

Among these promising approaches, one frequently mentioned method is the use of polyelectrolytes (PEs). PEs are a special class of charged polymers that are usually water-soluble. When oppositely charged PEs meet, they tend to complex into different forms.¹⁰ PEs are often used to build films using a layer-by-layer (LbL) approach, where a thin transparent polyelectrolyte multilayer (PEM) can be deposited on a charged substrate by repeatedly dip-coating the substrate into cationic and anionic PE solutions.¹¹ PEM-based films with added nanocomponents, such as nanoclays or graphene oxide, have demonstrated excellent gas barrier properties that lead to a >99% reduction in oxygen permeation.¹²⁻¹⁴ However, multicomponent films remain a substantial challenge for recycling. Without adding other components, PE-only films have also been constructed using LbL, and it was observed that the dense ionically cross-linked network also lowered the gas permeation significantly.¹⁵⁻¹⁸ The LbL approach is a straightforward method and has nanometer-level control over the film structure; however, the extensive film deposition and washing steps limit the possibility to scale up and industrialize.

A two-step film deposition method was developed by Haile et al. in 2017.¹⁹ Using two weak polyelectrolytes: polyethylenimine (PEI) and poly(acrylic acid) (PAA), pH and salt concentration were tuned to form liquid coacervates with
processible viscosities. The formed coacervates were then cast using a Meyer rod, after which stronger complexation and solidification were induced by immersion into a buffer bath. Compared with the LBL approach, this method is much more simplified. However, the composition and concentration of the coacervates remained unknown. In a more recent study, Smith et al. proposed a method to form a solution of poly-(diallyldimethylammonium chloride) (PDDA) and PAA. By adjusting the pH to 2, PAA remained uncharged and could thus be homogeneously mixed with PDDA. After the film formation by dip-coating, again a bath was used to induce complexation.\(^{20}\) The advantage of this solution-based approach is that the PE concentration and ratio could be controlled. For both methods, the aqueous immersion step provides the environment for introducing the necessary pH switch. It is a controlled procedure in which different parameters can be tuned, such as acid/base types, pH value, salt types, and their concentrations. However, the thickness is limited as once a dense top layer is formed, the lower part takes too long to be further complexed. Moreover, since PE chains may become mobile in the aqueous environment, it is difficult to detect whether the composition of the films remains the same as that of the initial preparation. For instance, excess polymer chains and salt ions can transfer from the coating into the bath.

In this work, we report a unique and simple one-step approach to the formation of a polyelectrolyte complex (PEC) film, with excellent control over the final film thickness and composition. PAA and PEI under normal pH conditions would complex in solution. However, by adding a volatile base, PEI becomes uncharged and can be mixed with PAA to form a homogeneous solution. Here, we use ammonia (NH\(_3\)), which is already commonly used in the paint and coating industries. High-concentration solutions with various ratios of PEI, PAA, and NH\(_3\) were prepared to study their phase behaviors. Here, we use branched PEI instead of linear PEI because commercially available linear PEI has low molecular weights, which is not suitable for the film formation, and because branched PEI has been well studied in the LBL system for various applications.\(^{3,22}\) Selected solutions were then cast using a Meyer rod onto biaxially orientated polypropylene (BOPP) substrates. During NH\(_3\) evaporation, the pH reduction allows the PEs to complex, leading to films that demonstrate excellent oxygen barrier properties as shown in Scheme 1. This method of controlling pH has several advantages over both the LBL approach and the aqueous bath approach. Films with different thicknesses can be prepared in a simple manner, while the top dense layer may slow down or stop the complexation in an aqueous bath. Moreover, coating various substrates is possible, including paper. Above all, the layer composition is well controlled beforehand, as all nonvolatile components become part of the complex layer. The final advantage of this one-step method is that by exposing the film to NH\(_3\), the films can be dissolved again. This reversibility makes recycling possible while the films can maintain their properties under normal conditions.

2. EXPERIMENTAL SECTION

2.1. Materials. Branched polyethylenimine (PEI, average M\(_w\) 25 000 g mol\(^{-1}\), ≤1% water), poly(acrylic acid) (PAA, average M\(_w\) 100 000 g mol\(^{-1}\), 35 wt % in water), ammonia (NH\(_3\), for analysis EMSURE ISO, Reag. Ph Eur, 25% in water), hydrochloric acid (HCl, ACS reagent, 37%), sodium hydroxide (NaOH, >98% pellets), sodium chloride (NaCl, ACS reagent, ≥99.0%), methyl red (ACS reagent, crystalline), and thymol blue (ACS reagent) were all purchased from Sigma-Aldrich (the Netherlands). All water used was deionized water (Milli-Q, Merck, the Netherlands). All chemicals were used as received. Biaxially orientated polypropylene (BOPP) sheets were provided by BASF and purchased from Hapec B.V., the Netherlands.

2.2. Preparation of Phase Diagrams.

2.2.1. Varying NH\(_3\) Concentration. PEI was diluted to 20 wt % using deionized water. PAA 35 wt % stock solution was first diluted with NH\(_3\) solution to 30, 25, and 20 wt %. Then, these solutions were further diluted to 20 wt % with deionized water. With this control, there were samples with four levels of NH\(_3\) concentrations including a blank. Different ratios of PEI/PAA were prepared from 4:1 to 1:3. The mixing ratio was based on the charge ratio such that every primary, secondary, and tertiary amine group of PEI was considered as a potential charge site, while PAA has one charge site per monomer (M\(_{\text{Hi}}\) = 43.04 g mol\(^{-1}\) and M\(_{\text{AA}}\) = 72.07 g mol\(^{-1}\)).

2.2.2. Varying PE Concentration. PEI 100 wt % stock solution was diluted with water to 35, 20, 10, and 5 wt %. PAA 35 wt % stock solution was also diluted with water to 20, 10, and 5 wt %. Four sets (35, 20, 10, 5 wt %) with different ratios of PEI/PAA mixtures were prepared following the same charge ratio.

2.2.3. Adjusting pH before Mixing. Three sets of different pH (5, 7, 9) samples were prepared. The pH of 20 wt % PAA and PEI were first adjusted to the same pH value 5, 7, or 9 by adding 5 mol HCl or NaOH. After reaching the desired pH, they were diluted to 10 wt % PE. Different ratios of mixtures were prepared.

All of the samples were stirred vigorously with a stirring bar for 15 min after which different phases of materials (homogeneous solution, coacervate, complex) were obtained. Photos of these phase diagram samples were all taken when the phases were stable (>48 h). Depending on the appearance of the mixtures, they were identified as a complex (solid in an aqueous phase), a coacervate (a liquid PE rich phase coexisting with a dilute phase), or a solution (one transparent phase). Then, the pH of each sample was measured using pH strips (pH 0–14 Universal indicator, Merck, the Netherlands). To obtain more accurate pH results, the eyedropper tool from Adobe Illustrator was used to extract colors for comparisons (Figure S1).

To visually track the pH changes, pH indicators were added into PEI/PAA 1:1 (thymol blue) and 1:3 (methyl red). For comparison, a
solution was added to the PEI solution at once. In total, 4 g of solution mixture was prepared for each ratio. Each solution was stirred vigorously with a stirring bar for 30 min and was judged ready for use when all bubbles had disappeared.

2.4. Film Fabrication and Thickness Control. BOPP substrates were cleaned with water and ethanol, then pretreated with an oxygen plasma (Femto plasma cleaner, Diener electronic GmbH, Ebhausen, Germany) to introduce hydrophilicity. To examine the control over charge ratios, PE films at a ratio of 1:1 were cast using a casting machine (BYK Instrument) with 10, 25, 50, and 100 μm Meyer rods. Triplicate samples for each thickness were prepared and all films were dried inside the fume hood. Another method to examine the overall thickness of the substrates was to weigh the dried films after removing the solvent completely (Quorum Q150T ES, Quorum Technologies, Ltd., U.K.).

2.5. Film Characterizations. Fourier transform infrared (FT-IR) spectroscopy (Spectrum Two, PerkinElmer) was used to examine pure PEIs (PAA, PAA with ammonia, PEI) and the mixed films. Freestanding pieces of PE films were prepared on a hydrophobic Teflon plate, followed by drying in the fume hood. To remove water, all samples were dried under vacuum at 30 °C for 24 h. The

Table 1. Composition and Calculated Density of PEI/PAA at Different Ratios

| charge ratios PEI/PAA | PEI (wt %) | PAA (wt %) | NH₃ (wt %) | H₂O (wt %) | calculated density of dried films (g·mL⁻³) |
|-----------------------|------------|------------|------------|------------|------------------------------------------|
| 4:1                   | 14.1       | 5.9        | 3.2        | 76.8       | 1.10                                     |
| 3:1                   | 12.8       | 7.2        | 3.8        | 76.2       | 1.12                                     |
| 2:1                   | 10.9       | 9.1        | 4.9        | 75.1       | 1.15                                     |
| 1:1                   | 7.5        | 12.5       | 6.7        | 73.3       | 1.22                                     |
| 1:2                   | 4.6        | 15.4       | 8.3        | 71.7       | 1.28                                     |
| 1:3                   | 3.3        | 16.7       | 8.9        | 71.1       | 1.31                                     |

measurements were conducted in the reflectance mode at a spectral resolution of 4 cm⁻¹ from wavenumber 400 to 4000 cm⁻¹. For each measurement, a minimum of 16 scans was conducted.

Film morphology and defects were examined by a scanning electron microscope (SEM, JSM-6010LA, JEOL, Japan). All samples were stored under vacuum at 30 °C for 24 h before imaging. To induce conductivity, a Pt/Pd 5 nm coating was sputtered on the samples (Quorum Q150T ES, Quorum Technologies, Ltd., U.K.). To show the film responses to water, dried freestanding pieces of PE films were put into deionized water and stirred for 5 min with a stirring bar. A 3:1 PEI/PAA oxygen permeation test sample was put into water and then ammonia to demonstrate the possibility of recycling.

2.6. Oxygen Permeation Test. The oxygen permeation of the films was measured by a gas separation setup. Samples were prepared on the previous day and stored in the fume hood. All measurements were performed at the same conditions at 30 °C and 0% relative humidity. The applied pressure was 3 bar. Before starting measurements, films were degassed under vacuum for 6 h. Each sample was measured for 48 h. The permeability is defined as barrier, shown in eq 2

where \( n \) (mol) is the amount of oxygen collected, \( d_{total} \) (m) is the thickness of the film, \( s \) (m²) is the surface area of the sample, \( t \) (s) is the time used for collecting \( n \) mol of oxygen, and \( P \) is the pressure difference.

The amount of gas collected in a certain volume was controlled by setting the end pressure, based on the ideal gas law (eq 3)

where \( P_{end} \) was set to be 2 mbar; \( P_{start} \) should be around 0 (under vacuum), then the unit of pressure was converted to Pa; \( V \) (m³) is the cell volume, \( R \) is the ideal gas constant 8.3145 m³·Pa·K⁻¹·mol⁻¹, and \( T \) (K) is the temperature (303.15 K).

For the final permeation data, the system leakage was considered and excluded from the raw data. The leakage rate was around \( 2 \times 10^{-5} \) mbar·s⁻¹, with small variations among four different cells. Samples of bare BOPP sheets, single PEI, single PAA, and mixed films at six different ratios were measured. For each data point, at least three samples were measured, and the average results with standard deviations were reported. The permeation data in barrier were also converted into OTR (cm³·m⁻²·day⁻¹·atm⁻¹) for comparisons (eqs S1 and S2).

3. RESULTS AND DISCUSSION

3.1. Phase Diagrams. To characterize PE complexation, its phase behavior was studied. PE mixtures can exist as a solution, coacervate, or solid complex depending on various parameters, such as pH, PE concentration, mixing ratio, and salt concentration.²³ For our application, the transition from a homogeneous solution to a solid complex is the key. Here, we use high-concentration solutions instead of coacervates for several reasons. Coacervates are not homogeneous right after mixing and it can require days or even weeks for them to stabilize. The formed coacervates have high viscosities that make casting difficult and they cannot be diluted with water to control the viscosity. Adding water to coacervates again leads to phase separation. Most importantly, the composition and the concentration of the coacervate remain unknown. Thus, we focus on solutions that can be homogeneously mixed with a controlled ratio. To form a continuous film, rather than separated particles, the concentration should be high to ensure a continuous network throughout the drying process.
Many phase diagrams in the literature have proven that the PE phase can be tuned from a solution to a solid complex by varying PE concentration, PE molecular weight, PE mixing ratio, salt concentration, and using miscible solvents. Surprisingly, there is no thorough study of pH-induced phase transitions, even though pH is one of the most important parameters for tuning weak polyelectrolytes. The complexity of adjusting pH is that the salt concentration would usually also change. Sun et al. were the first to demonstrate a successful phase transition of PEI and PAA by tuning pH. In our chosen system, both PEI and PAA were used in their uncharged forms without other counter-ions, while the pH was tuned by NH₄⁺ which gave us a system only containing ammonium ions (NH₄⁺). This is important because in our one-step film deposition method, introducing salt ions may lead to salt crystallization/inhomogeneity during drying. An example of possible defects is shown in Figure S2. Thus, phase diagrams with varying NH₃ concentration and PE concentration were constructed.

First, the effect of the NH₃ concentration for mixtures prepared at different ratios was studied, since pH is a crucial parameter that influences the degree of ionization of both PEI and PAA. Pictures of the samples at different pH and mixing ratios are shown in Figure S3. Figure 1a shows that a homogeneous solution phase can be achieved for each ratio when sufficient NH₃ (no higher than 5 wt %) is added. As the NH₃ concentration decreases, there is a phase transition from solution to coacervate (PEI/PAA ratios 4:1−2:1) or solution directly to solid complex (ratios 1:1−1:3). For the film formation, the solutions with the highest concentration of NH₃ were used. As NH₃ evaporates, the final film composition would be expected to follow the same transitions. This indicates that most ratios can reach the dense complex state that is desired for gas barrier properties.

The pH of the different samples (in Figure 1b, the same data are replotted) was obtained using pH indicator paper because a pH electrode could not be used due to the high viscosity of the samples. Since the smallest pH difference that can be detected with these universal pH paper strips is approximately one pH unit, the accuracy is limited. For example, both solution and coacervate phases were found for a polymer ratio 4:1 at pH 11. Probably, the pH change required for this transition is too small to be detected. PEI and PAA are both weak polyelectrolytes so that pH directly influences their degree of ionization. PAA has a pKₐ value around 4.5, and when the pH is around 2 it is not charged, while at a pH reaching 10 it becomes fully charged. The branched PEI has three different pKₐ values due to its primary (4.5), secondary (6.7), and tertiary (11.6) amines. Oppositely to PAA, PEI is fully charged at low pHs (<4) and almost uncharged at high pHs (>10).

In general, our phase diagram shows that the complexity is successfully avoided by keeping PEI almost uncharged at high pH around 10−11, while complexation occurs at lower pH, where both PEI and PAA are charged. There is also a clear effect of the mixing ratio, with high PEI/PEA ratios (4:1−2:1) complexing at substantially higher pH values than the low PEI/PAA ratios (1:1−1:3). Most likely PEI remains partially charged even at a pH of 10, still allowing macroscopic phase separation when there is a sufficient excess of PEI. However, when PAA is in excess, the pH has to be sufficiently low for PEI to induce macroscopic phase separation. Otherwise, small negatively charged soluble complexes may be formed with one PEI chain interacting with a few PAA chains present in the solution.

Next, the effect of PE concentration on the phase behavior was studied, to determine whether the evaporation of water would also be able to induce a phase transition. Pictures of the samples and measured pH values are shown in Figure S4. The PE concentration range studied starts at 5 wt % and ends at 35 wt %, due to viscosity limitations. Within this concentration range of 5−35 wt %, no phase transition was observed. As shown in Figure 2a, samples at PEI/PAA ratios 4:1−2:1 all formed coacervates while from 1:1 to 1:3 they formed solid complexes. This indicates that water evaporation alone cannot trigger a phase transition when concentrating PEs from 5 to 35 wt %. It is noticeable that for excess PEI ratios, complexes were first formed; then, they turned into a coacervate. For example, the PE phase was between a complex and a coacervate for ratio

![Figure 1](https://doi.org/10.1021/acsami.1c05031)
2:1 at 35 wt %. Our data do not exclude the occurrence of phase transitions when the PE concentration exceeds 35 wt %. It is possible that when the PE concentration exceeds a certain value during drying, the chains may be “quenched” in the complex form due to a loss of mobility.

The pH values of the various samples are also replotted in Figure 2b to connect the pH value to the obtained phase. Interestingly, even at pH 11, the ratios 4:1, 3:1, and 2:1 were able to form a coacervate or complex instead of a solution at high polymer concentration. One explanation is the limited accuracy of pH measurements. Another is that the additional NH$_4^+$ helps to avoid complexation by charge screening. Apart from that, these data are consistent with the first phase diagram (Figure 1), showing that the mixtures with excess PEI form coacervates, while the ratios with excess PAA form solid complexes at sufficiently low pH.

To study the complexation, while eliminating the effect of pH change, PEI and PAA solutions were adjusted to the desired pH (5, 7, 9) before mixing. Within this phase diagram (Figure 3), the effect of added HCl or NaOH on the salt concentration was neglected, as the pH is expected to have a stronger influence compared to the small changes in salt concentration that stem from setting the pH. These three pH values were chosen because they correspond to cases where PEI and PAA are almost equally charged (pH = 7), where PEI is more charged than PAA (pH = 5), and where PEI is less charged than PAA (pH = 9). The pictures of the samples and the pH of the mixtures are included in Figure S5. Comparing samples with the same pH, coacervates were formed when PEI was in excess for pH = 7 and 9, while for pH = 5, solid complexes were formed at all ratios, probably because of the higher charge density of PEI. Using the ratio 1:1 as an example, an acidic environment is required again to ensure that PEI is sufficiently charged. One difference compared to the previous observations is that at a ratio of 1:1 at pH 7, a solid complex was formed in previous phase diagrams while here it is a coacervate.

Summarizing all three phase diagrams, it can be concluded that excess charged PEI is required to form a solid complex. This can be achieved in two ways, either by increasing the PEI concentration at fixed pH or by decreasing the pH at fixed PEI concentration. This result is in agreement with the study of Sun et al., who found that solid precipitates (“nonfluidity state”) formed when the pH was low enough (~4) or when PEI was in excess. They also proposed a structural rearrangement of the premixed complex into a precipitated complex, either a turbid colloidal suspension or one phase soluble complex depending on the PEI/PAA ratio and pH.$^{30}$ The difference with our study is that we used PEI and PAA with much higher $M_w$, which enhances the macroscopic phase separation. Combining with our pH data, the possible structural changes are summarized in Figure 4. Due to the branched nature of PEI and the difference in $M_w$, the PAA chain acts as the long backbone, while PEI as more compact coils.$^{37}$ For a fixed ratio, PEI gets less charged and PAA gets more charged when pH increases. The solid complex then acquires a net negative charge, which weakens the interaction and leads to a liquid-like coacervate and eventually to soluble complexes. Eventually, when the pH is too high, the complexes fall apart because the electrostatic attraction vanishes when PEI becomes uncharged. For a fixed pH, the ratios with more PEI are more likely to form a precipitate. The circled samples in Figure 4 showed more than one phase behavior at the same pH; one possible reason can be the limited accuracy in the pH measurements. Another reason can be the difference in salt concentrations. At pH 11, the samples from phase diagram 1 appeared as solutions due to the presence of NH$_4^+$, while the samples from phase diagram 2 (zero salt ions) appeared as coacervates. A similar case occurred for the samples at pH 7 that the sample from phase diagram 3 (containing Na$^+$ and Cl$^-$) appeared as coacervate, while the other two samples from phase diagrams 1 and 2 appeared as complex.
Translating the information obtained from the phase diagrams to the proposed drying process, it can be expected that the phase transitions during drying are dominated by NH₃ evaporation and the resulting decrease of the pH. Although water evaporation happens simultaneously, it only concentrates the PEs without inducing phase transitions in the studied range 5−35 wt %

Once NH₃ has completely evaporated, the pH returns to the original pH. This starting pH was predetermined by the mixing ratio. The pH at every ratio was therefore different due to the acidity of PAA and the basicity of PEI. This explains why 4:1 and 3:1 ratios, with excess PEI, can only form coacervate because excess PEI also increases the pH. To monitor whether the expected decrease of the pH occurs during drying, pH indicators were used to track the pH change during the drying process (Figure S6). For PEI/PAA ratios 1:1 and 1:3, the pH required for solid complexation was indeed reached. By contrast, when the nonvolatile base NaOH was used to adjust the pH, the pH did not decrease. The videos of the drying processes are also available in the Supporting Information (Videos S1 and S2).

3.2. Film Preparation and Characterization. To show control over the thickness of the films, PE films at a ratio of 1:1 were prepared using different Meyer rods (wet 10, 25, 50, and 100 μm thick). Figure 5 shows that the dried film thickness increases linearly with increasing Meyer rod thickness. The solutions used contain an overall 20 wt % PE and the final dried film thickness should therefore be around one-fifth of the wet thickness. Indeed, the thicknesses measured by a micrometer were similar to these values. However, when comparing the measured film thicknesses with the calculated thickness, assuming the densities reported in Table 1, the measured thickness is approximately 30% higher. This indicates that residual water remains trapped in the films, because of the hydrophilic nature of the PEs. To avoid film damage before the permeation test, thicknesses of the samples were estimated by calculation. We postulate that the final thicknesses are close to the calculated ones in these experiments because these measurements were done at 0% relative humidity, where residual water will evaporate.

During drying, mechanical stresses can develop in the polymer film due to water loss, which can lead to film damage. This is more likely to occur for thicker films. Films prepared with a 50 μm rod, except those at ratios 4:1 and 3:1, all showed cracking while handling, while the top layer of the film prepared at a ratio of 3:1 was delaminated from the BOPP support after the oxygen permeation test. This may result from the measuring condition at 0% relative humidity and continuous gas flushing. For films prepared with a 25 μm rod, the delamination was avoided but microcracks were observed (Figure S7). For the thinnest films, prepared using a 10 μm rod, no cracks were observed at any of the PE ratios. Therefore, these films were used for oxygen permeation tests. The development of mechanical stresses was also apparent from the tendency of films to bend after detaching from the substrate. As shown in Figure S8, films prepared with only PEI or PAA and films containing an excess of PEI showed little curling, while films prepared with excess PAA curled up.
significantly, indicating large stresses in these films. This is in agreement with the phase diagram in Figure 1, which shows that films with excess PAA formed solid complexes, which cannot relax mechanical stresses, contrary to films with excess PEI, which stay liquid-like during most of the drying process.

Infrared spectroscopy was utilized to examine the dried PE films. For comparison, single PEs were also measured as dry samples. Pictures of freestanding films of PAA, PEI, and PEI/PAA at a ratio of 1:1 are shown in Figure S9. PAA is known to absorb ammonia under ambient conditions, and thus some ammonium ions NH$_4^+$ may remain in the film. However, FT-IR results (see the Supporting Information) cannot prove whether there was residual NH$_4^+$. In fact, the films are a mixture of PEI and PAA in both charged and uncharged forms so that the exact composition of the films cannot be determined from FT-IR spectra.

The transparency of the coated BOPP film is demonstrated in Figure S10. The overall film quality and structure were examined by SEM before the oxygen permeation tests. All PE films dried as a dense layer, and no pores were observed (Figure S11). During the film formation, it was observed that indentations from the wires of the Meyer rod can be generated. As shown in Figure 6, all films appeared to have good film coverage. PAA showed some hole defects that can be caused by dewetting. For the different PE ratios, some inhomogeneities could be caused by fast NH$_3$ evaporation. The viscosity of the solution starts to increase immediately due to the onset of the transition to coacervate or complex. This could cause a leveling problem as the indentation from the wires may present. The defects of the BOPP substrate or dust particles can also lead to other small defects like pinholes and cracks (Figure S11). The number of these defects was, however, small and only a limited impact is expected on the overall barrier properties. For the oxygen permeation tests, only the good areas with no visible defects were used. The observations were repeated after the oxygen permeation measurements. No visual cracks of the films were observed, indicating that the layers were stable during the oxygen barrier experiments.

The proposed approach indeed leads to the formation of an optically transparent coating. To demonstrate that the layer consists of PEC instead of dried PEs, some freestanding pieces of the films were obtained and were put into deionized water to examine whether they dissolve or not (Figure S12). For the PEI/PAA ratios 4:1–2:1, the films did not dissolve, clearly indicating complex formation. After stirring, the films became swollen and turned white, similar to previous observations for polyelectrolyte multilayers based on similar PEs; this can be explained by the formation of water pockets that leads to a porous structure. However, for the ratios 1:1–1:3, the films did dissolve in water. The excess of negative charge allows for the formation of soluble complexes, resulting in the removal of the films. Finally, one sample with 3:1 PEI/PAA was first exposed to deionized water, leading to swelling of the coating, after which it was exposed to a 5 wt % NH$_3$ solution where the film dissolved completely. This reversible complexation process makes it possible to recycle such PE-based films and their plastic supports, which is an advantage over current oxygen barrier coatings.

### 3.3. Oxygen Barrier Properties

To understand the relationship between film composition and oxygen barrier properties, the oxygen permeation through films consisting of pure PEI or PAA, as well as films with different ratios of PEI:PAA was measured. The permeation of gas through a dense film is mainly dependent on the solubility of the gas molecules in the film and their diffusivity through the film. When both solubility and diffusivity are minimized, the film should be a good gas barrier. In our case, PAA is more polar than PEI, and as such, the PAA film should have the lowest solubility for nonpolar oxygen. However, the structure of the film also matters and there should be an optimal ratio at which the complexation of the film is maximized to give the densest network structure. The oxygen permeability of bare BOPP substrate was 0.7212 ± 0.0712 barrer (OTR 1666 ± 169 cm$^3$ m$^{-2}$ day$^{-1}$ atm$^{-1}$), in line with the literature. All coated BOPP films showed significantly improved oxygen barrier properties as shown in Figure 7. Surprisingly, pure PEI films gave lower permeation than pure PAA films. A possible explanation is that pure PEI is sticky and that it has the best adhesion with both BOPP and the O-rings that were used for sealing. The drawback is that the prepared PEI film was difficult to handle, and that extra caution was required not to damage the film. On the other hand, pure PAA has the highest permeation and also the largest error. As shown in the SEM images (Figure 6), pure PAA showed dewetting behavior and the coverage of the films may not be as good as for the other films. The relatively poor film quality led to relatively high permeation and poor reproducibility. Interestingly, all PEI/PAA films showed low permeabilities. There is no clear trend between the permeability and the PEI/PAA ratio, but all films have excellent barrier properties. No significant differences in the permeability could be observed between films with excess PEI (which forms coacervates) and films with excess PAA.
Figure 7. Oxygen permeability and OTR results of single PEs and different ratios.

(which forms solid complexes). The lowest permeability (no permeation could be detected with our setup, <0.002 barrer) was found from films with a ratio of 2:1. After the measurements, the thicknesses of the samples were measured using a micrometer and the errors were within 1 μm.

The permeability data were also converted into OTR to compare with the literature that our lowest OTR is below 4 cm³·m⁻²·day⁻¹·atm⁻¹, placing it clearly in the domain of oxygen barrier coatings. According to the literature, it can be used as a gas barrier for products such as oil, snacks, or meat, also depending on the water vapor permeance. The advantages of this one-step method are: (1) The formed PEC films (ratios 4:1–2:1) are much less water-sensitive compared to pure PE. (2) The ratio of PEI/PAA allows tuning of properties such as gas barrier and mechanical strength. (3) This approach allows the use of paper as a substrate. It is true that our one-step layer did not give as low oxygen permeability as observed in the literature for multistep approaches (0.013 for PDDA/PAA, 0.079 for PEI/PAA). Despite the use of completely different measuring methods and a better oxygen barrier substrate PET that they used, one major reason can be the lack of curing steps. In the literature, a low-pH bath and curing after deposition were provided to allow the films to rearrange. Here, a pH trigger was induced such that the final film pH was predetermined by the mixing ratio. For ratios 4:1–2:1, the basicity of PEI causes an unfavorable pH for complexation as PEI is barely charged. This shows that there is certainly potential for our approach to achieving even better barrier properties through further optimization.

4. CONCLUSIONS

In this study, we have demonstrated a novel single-step approach to fabricate thin PEI/PAA complex coatings using NH₃ evaporation as a trigger. The pH was first raised to neutralize PAA and uncharge PEI to prepare a homogeneous solution. Then, the pH decrease by evaporation of NH₃ and the charging of PEI by protonation leads to the desired complex formation with PAA. Phase diagrams provided us insight into where the phase transitions start. Homogeneous solutions with known concentrations and ratios were successfully prepared for film formation. Compared to uncoated BOPP, all PE films showed improved oxygen barrier properties. The best film with a PEI/PAA ratio of 2:1 has the lowest permeabilities that they could not be detected by our setup (<0.002 barrer, OTR < 4 cm³·m⁻²·day⁻¹·atm⁻¹). The work described here shows that employing volatile bases can provide a completely new route toward PEC films. For the first time, this eliminates the need for tedious and impractical bathing steps and opens the door for real-world, industrial application of these unique materials. On top of this, the excellent oxygen barrier properties make the PEI and PAA complex a promising recyclable barrier material for flexible food packaging. For the following work, we are working on other polyelectrolyte combinations, which may bring better properties and new functionalities. Finally, we see many possibilities to further improve such one-step coatings, for example, with post-treatments. Although the formed films under ambient conditions can be handled without generating cracks or delamination, the mechanical properties of the films are sensitive to any humidity change. Various cross-linking approaches and the addition of plasticizers or nanocomponents can be utilized to further improve the mechanical stability of the films if required. Many directions can be explored to further deepen and exploit this novel approach and eventually on the macroscale.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c05031.

Method to determine pH values, conversion from barrer to OTR, possible salt crystallization defects, original pictures of phase diagrams and their pH values, tracking pH changes with pH indicators, cracking of thicker films, different curling levels, IR of all PEC and single PEs, possible film defects, transparency of the film, and recyclability of the samples (PDF)

Video of the drying process of a PEI/PAA 1:3 film containing the pH indicator methyl red (MP4)

Video of the drying process of a PEI/PAA 1:1 film containing the pH indicator thymol blue (MP4)

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