Synthesis and Characterization of Solution-Processable Polyelectrolyte Complexes and Their Homogeneous Membranes

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ABSTRACT Solution-processable polyelectrolyte complexes (PECs) between poly(diallyldimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA) were synthesized in aqueous NaOH and obtained in their solid forms by protection and deprotection of carboxylic acid groups. Elemental analysis, conductance measurement, and FT-IR showed that the composition and ionic complexation degree (ICD) of the PECs can be controlled effectively by tuning the NaOH concentration in both parent polyelectrolyte solutions. Thermal gravity analysis showed that PECs revealed good thermal stability, and differential scanning calorimetry showed that the glass transition temperature (T_g) of PECs increased with increasing ICD and finally became undetectable when ICD was above 0.16. Viscosity properties of the PEC solutions were well correlated to the ICD of PECs, and it was found that solid PECs could be redissolved in dilute NaOH without breaking the ionic complexation between PDDA and PAA. Homogeneous PEC membranes (HPECMs) were made from their concentrated solutions, and their morphologies were examined by field emission scanning electron microscopy. These novel HPECMs were subjected to dehydration of organics for the first time, and a very promising performance was obtained. Furthermore, another two solution-processable PECs between weak anionic polyelectrolyte and cationic polyelectrolyte were also synthesized by the same method and showed a very high separation performance.

KEYWORDS: polyelectrolyte complex membrane • viscosity property • thermal property • pervaporation

INTRODUCTION

Polyelectrolyte complexes (PECs) between oppositely charged polyelectrolytes have gained increasing interest since pioneering work by Michaels et al. (1). Because of the biological relevance of PECs (2), research in this field has recently flourished and many researches have focused on the fundamentals concerning the formation of PECs (3) and the synthesis of PEC nanoparticles (4) and water-soluble PECs (5, 6). The application of PECs includes flocculants (7), vehicles for gene delivery (8), and microencapsulation (9), all of which take place in liquid media. PEC solids are generally infusible and insoluble in a common solvent (5) without breaking the ionic interaction inside them, and hence it is notoriously difficult to process them. Aimed at overcoming this problem, strategies for synthesizing water-soluble PECs have been established by using a block copolymer containing a neutral hydrophilic chain segment. However, the obtained PECs are soluble only at low concentration, and the method is apparently not applicable for processing PECs conveniently on a large scale (5). Because of this, researches concerning the physicochemical properties of PECs in solid form remain undeveloped (10) and applications of PECs as solid materials are rather rare (11).

Membranes and films, as important forms in which solid materials are usually used (12, 13), have by far been the one and only form in which solid PECs are used. There have been methods for fabricating the "so-called" PEC membranes or films in the literature. Smitha et al. (14) have explored poly(acrylic acid) (PAA)−chitosan PEC membranes for fuel cell application by the blending method. By this method, concentrated solutions of PAA and chitosan were respectively prepared in acid and then blended. This method was also used to fabricate PEC membranes for pervaporation (15−18) or for testing of the bulk properties of PEC films (19). Richau et al. (20) have introduced the interfacial reaction method to fabricate "two-ply" PEC membranes, in which one polyelectrolyte solution was first cast onto a microporous substrate and another polyelectrolyte solution was subsequently cast or spin cast onto the surface of the former polyelectrolyte layer. Lim et al. (21, 22) mixed chitosan and sodium alginate and cast their coacervates to fabricate PEC membranes for coating and wound dressing. It can be seen that, even though these methods artfully avoid the direct processing of solid PECs, there are still some important aspects to improve. For the blending method, the charge density of a weak polyacid in concentrated acid is very low and hence interaction between component polyelectrolytes should be very weak. That is to say, the mixing of two polyelectrolyte solutions is more like a physical

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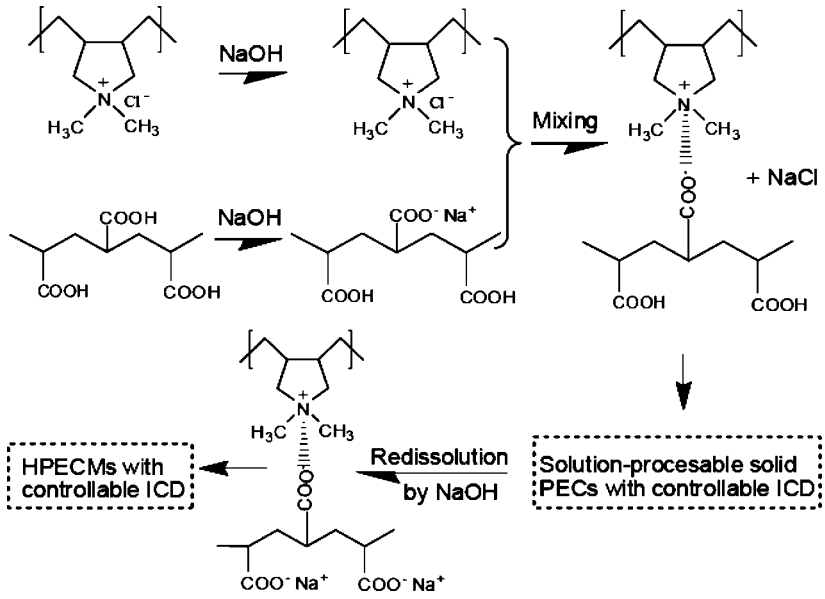
Scheme 1. Schematic Diagram for Fabrication of PDDA−PAA HPECMs with Controllable ICD



solution blending of neutral polymers but not ionic complexation, and hence the obtained membrane is not a real PEC membrane but more like a blend membrane. For the interfacial reaction method, the composition and ionic complexation degree (ICD) of PEC at the interface is out of control and the obtained membrane is inhomogeneous; i.e., theoretically there are three layers along its cross section, and PEC forms just a thin layer at the interface of two polyelectrolytes. Furthermore, the small ions emitted during complexation at the interface are not wanted and unfortunately cannot be eliminated from the membrane. For the coacervation method, the ICD is also out of control and it is not easy to control the structure of the obtained PEC. However, to our knowledge, these are the only methods available for fabricating these "so-called" PEC membranes or films up to now. So, in order to explore the application of solid PEC materials, it is quite needed to develop a new method, by which homogeneous membranes made of solid PECs with controllable ICD can be obtained.

In this study, our aim is to propose a facile and universal method for synthesizing solution-processable PECs with controllable ICD and fabricating their homogeneous membranes. Furthermore, the separation ability of the membrane was evaluated by pervaporation, which is a promising liquid−liquid molecular separation technique because of its high efficiency and energy savings (23−25).

EXPERIMENTAL SECTION

Materials. Poly(diallyldimethylammonium chloride) (PDDA; M_w = 70 000 g/mol, 20% aqueous solution) was obtained from Aldrich and used as received without further purification. Poly(acrylic acid) (PAA) was made in our laboratory through traditional radical polymerization with a viscosity-average molecular weight of 750 000 g/mol determined by viscometry. A polysulfone ultrafiltration membrane was obtained from the Development Centre of Water treatment technology, Hangzhou, China. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) are analytical reagents and were obtained from the Shanghai First Reagent Co. Deionized water with a resistance of 18 MΩ cm was used in all experiments.

Synthesis of Solution-Processable PECs. ***Theoretical Principles.*** A weak polyacid and a strong cationic polyelectrolyte usually form nonstoichiometric PECs, and their compositions can be tuned by controlling the pH value of the component polyelectrolyte solutions. These PECs, if formed in NaOH of proper concentration, have residue un-ionized carboxylic acid groups in them. By ionization of these carboxylic acid groups, PECs are soluble in aqueous NaOH, and hence it is possible to fabricate a homogeneous PEC membrane (HPECM) by solution-casting. In detail, PDDA and PAA were selected to fabricate HPECM, the protocol of which was illustrated in Scheme 1. It can be seen from Scheme 1 that the composition of PEC can be controlled by tuning of the NaOH concentration in a parent solution of both PAA and PDDA. The composition of PEC is expressed by the mole ratio of PDDA monomer to PAA monomer (M_{PDDA}:M_{PAA}). Besides, the ICD of PECs is defined as the ratio of the numbes of ionized carboxylic acid groups that have ionic interaction with PDDA to the total number of carboxylic acid groups in PECs. Theoretically, the ICD of PEC equals the value of M_{PDDA}:M_{PAA}. Experimentally, M_{PDDA}:M_{PAA} can be determined through the equation $M_{PDDA}:M_{PAA} = V_E/V_0$, where V_E is the volume of the PDDA solution added into the PAA solution until the end point of complexation and V_0 is the volume of the PAA solution used for the complexation (noting that the monomer concentration of both PAA and PDDA in the parent solution is the same). This is because PDDA chains added before V_E were incorporated into the PEC and those added after V_E were not incorporated. Determination of the end point could be realized by monitoring the conductance of the PAA solution versus the PDDA dosage. This is because the ionic complexation between PDDA and PAA emits small ions of Na^+ and Cl^-, which increases the conductance of the PAA solution. So, the inflection at the conductance−PDDA dosage curve indicates the reaching of the end point.

Experimental Process. PDDA and PAA were dissolved in deionized water (or NaOH of a given mole concentration) respectively with their monomer mole concentration equal to 0.018 mol/L. The PAA solution was equipped with a conductance recorder, and the PDDA solution was added into the PAA solution dropwise through a base burette under vigorous stirring after both PAA and PDDA were well dissolved. The PAA solution turned turbid immediately upon the addition of the PDDA

solution, and the turbidity increased as more PDDA solution was added into the PAA solution. Addition of PDDA was stopped when the end point was reached, where a macroscopic flocculation occurred, a large amount of PEC precipitated from the solution instantaneously, and the conductance did not change. These precipitates were taken out, rinsed by deionized water three times, soaked in a large amount of deionized water for 24 h to remove residual small ions, and then dried under vacuum at 50 °C. The final product of PEC was a yellowish hard solid. For the sake of simplicity, PECs with different compositions were named PEC*X* and their membranes were accordingly named as HPECM*X*, where *X* is its value of M_{PDDA}:M_{PAA} obtained from elemental analysis (EA). *X* also equals the value of the ICD. It should be noted that another two solution-processable PECs of PDDA-CMCNa and CS-CMCNa were also synthesized, and the experimental procedure is given in the Supporting Information.

Characterization. The FT-IR spectrum of solid PECs was obtained with a Bruker Vector 22 FT-IR spectrometer (Berlin, Germany) by dispersion of solid PECs in KBr and the creation of slices. FT-IR for HPECMs was done by casting of the concentrated solution of PECs on a KBr slice to obtain on it a very thin layer. EA was operated on a Flash EA1112 instrument (Thermofinnigan, Rodano, Italy). The morphology of the HPECM was examined with a field emission scanning electron microscope (FESEM; FEI Sirion-100, Hillsboro, OR). Differential scanning calorimetry (DSC) was obtained with a Perkin-Elmer Pyris 1 DSC (Waltham, MA) under a nitrogen atmosphere at a heating rate of 10 °C/min from 60 to 160 °C after elimination of the samples' heat history. Thermal gravity analysis (TGA) was obtained with a Perkin-Elmer Pyris 1 TGA at a heating rate of 20 °C/min from 50 to 700 °C. Viscosity measurements were carried out with an Ubbelohde dilution viscometer at 30 °C. The flux time was recorded within an accuracy of ±0.1 s. An extrapolation procedure according to the Huggins viscosity equation $\eta_{sp}/c = [\eta] + k_H[\eta]^2c$ was used to evaluate the intrinsic viscosity $[\eta]$ and k_H of PECs. For PECs with different ICDs, the mole concentration of NaOH in the solvent is different and is determined by the equation [NaOH] = [PAA](1 − M_{PDDA}:M_{PAA}), where [PAA] is the mole concentration of the PAA monomer and is calculated from the mass concentration of PECs and its M_{PDDA}:M_{PAA} value. In this way, theoretically there were no free NaOH ions in the PEC solution. Furthermore, the pH value of the PEC solution was about 8, confirming the validity of this equation. If this solution were to be diluted by 0.01 M NaCl, the NaCl mole concentration in the starting solution of PEC was also preadjusted to 0.01 M.

Membrane Preparation. On the basis of the solubility of PECs in NaOH, five PEC samples with ICDs in the range of 0.11−0.29 were chosen to fabricate their HPECMs and named as HPECM0.11, HPECM0.13, HPECM0.16, HPECM0.23, and HPECM0.29. A total of 0.25 g of PECs was dissolved in NaOH for 24 h with gentle stirring to form even solutions. For PECs of different ICDs, the mole concentrations of NaOH in the solvent were different and determined by the same equation: [NaOH] = [PAA](1 − M_{PDDA}:M_{PAA}). So, theoretically there were also no free NaOH ions in the casting solutions and HPECMs. HPECMs were fabricated by casting of the solution with an applicator on a clean and smooth porous polysulfone ultrafiltration membrane and drying at 40 °C for 8 h. Subsequently, the membrane was dried for another 12 h at 50 °C under vacuum to eliminate any residual water molecules. Pervaporation experiments of HPECMs were done in the same way as was reported previously (26).

RESULTS AND DISCUSSION

Synthesis of PECs with Different Compositions. Figure 1 gives the evolution of the conductance of the PAA solution versus the PDDA dosage during complexation at two NaOH concentrations of 0.0 and 0.006 M, respectively. It can be seen from Figure 1 that conductance first increases linearly with increasing PDDA dosage and then inflection appears at different PDDA dosages for 0.0 and 0.006 M NaOH. The linear increase of conductance is obviously due to the emitting of free NaCl ions during complexation between PDDA and PAA, and the inflection indicates the end point of ionic complexation. Thus, the M_{PDDA}:M_{PAA} value can be calculated through the equation M_{PDDA}:$M_{PAA} = V_E/V_0$, where the value of V_E at different NaOH concentrations can be directly read from the end point given in Figure 1. Table 1 gives the exact M_{PDDA}:M_{PAA} values of PEC samples determined by both the conductance method and EA. It can be seen that the values of M_{PDDA}:M_{PAA} determined by both methods are quite close to each other and increase with an increase in the NaOH concentration in parent polyelectrolyte solutions. This is because the ionization degree of the parent PAA increases with an increase in the NaOH concentration, because of which more PDDA is needed for neutralization of a fixed amount of PAA. Therefore, it is obvious that a high M_{PDDA}:M_{PAA} value also means a high ICD because in this case more ionized carboxylic acid groups are available on PAA chains for complexation with PDDA.

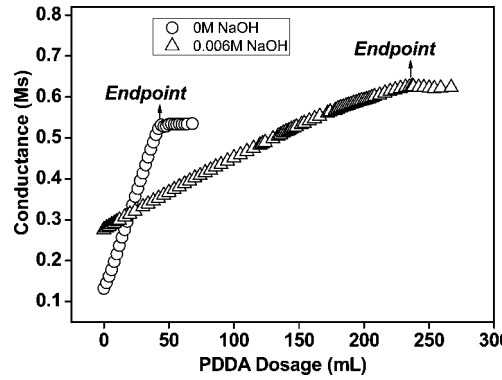


FIGURE 1. Plot of the conductance of the PAA solution versus PDDA dosages during the complexation process at two NaOH concentrations.

Table 1. Compositions of PECs Obtained by the Conductance Method and EA

		M_{PDDA}:M_{PAA}	
PEC sample	[NaOH] (mol/L)	conductance	EA
PEC0.11	0	0.12	0.11
PEC0.13	0.001	0.13	0.13
PEC0.16	0.002	0.15	0.16
PEC0.23	0.003	0.23	0.23
PEC0.29	0.004	0.30	0.29
PEC0.30	0.005	0.41	0.39
PEC0.55	0.006	0.58	0.55

Figure 2 shows the FT-IR spectrum of PEC0.11, PEC0.16, HPECM0.16, and PAA, respectively. Because ν(C═O) in unionized carboxylic acid groups has an absorption band at 1714 cm^{-1} and it shifts to 1580−1600 cm^{-1} upon ionization of carboxylic acid groups (27), this shift can be used to follow the state of carboxylic acid groups in parent polyelectrolytes, PECs, and HPECMs. In the curve for PAA, an absorption

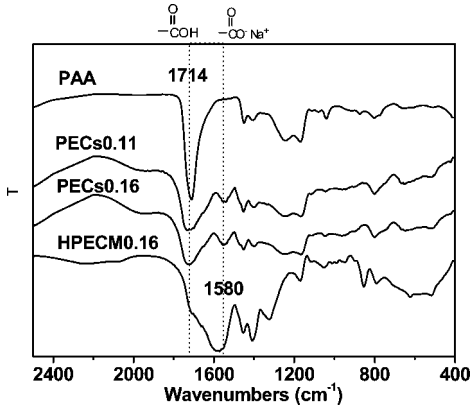


FIGURE 2. FT-IR spectra of PEC0.11, PEC0.16, HPECM0.16, and PAA.

band is observed only at 1714 cm^{-1} and it is assigned to ν(C═O) in un-ionized carboxylic acid groups on PAA chains. In curves for PEC0.11 and PEC0.16, there are absorption bands at both 1714 and 1580 cm^{-1}, which are assigned to ν(C═O) in un-ionized carboxylic acid groups and ionized carboxylic acid groups, respectively. This is because only part of the carboxylic acid groups on PAA chains were ionized after the the addition of a designed amount of NaOH, and there were both un-ionized carboxylic acid groups and ionized carboxylic acid groups in both PEC0.11 and PEC0.16. Obviously, the coexistence of absorption bands at 1580 and 1714 cm^{-1} confirmed the ionic complexation between PAA and PDDA. It also can be seen that the intensity ratio of 1714 to 1580 cm^{-1} for PEC0.11 is larger than that of PEC0.16. This is because the ionization degree of PAA in water is lower than that in 0.002 M NaOH. In the curve for HPECM0.16, the absorption band at 1714 cm^{-1} is almost not seen and absorption at 1580 cm^{-1} becomes much stronger. This obviously confirms the ionization of un-ionized carboxylic acid groups in PEC0.16 by a NaOH solvent, which is the last step in Scheme 1.

Thermal Properties of PECs. The thermal stability of a polymeric material is always a crucial issue and requires consideration, especially in the case of engineering application above room temperature. Figure 3 gives the TGA and differential thermal analysis (DTA) results of PECs, PAA, and PDDA, respectively. From parts a and b of Figure 3, it can be seen that there are roughly three major weight loss stages for PECs around 50−230, 230−340, and 340−525 °C in the tested temperature range. The weight loss that takes place in the first stage is 3.5 wt %, and the lost components are mainly small molecules such as physically absorbed water. The weight loss in the second stage is around 27 wt %. Besides the chain cleavage, it is considered that the weight loss in this stage also contains the structure water, which is confined in the ionic cross-linked PEC aggregates, and hence requires a high temperature for its release (27). It can be seen from Figure 3b that the chain cleavage rate for PEC is faster than that for both PAA and PDDA in the temperature range from 230 to 320 °C. This phenomenon was also observed with PECs between chitosan and carboxymethyl cashew gum (28, 29) and is probably because the ionic complexation

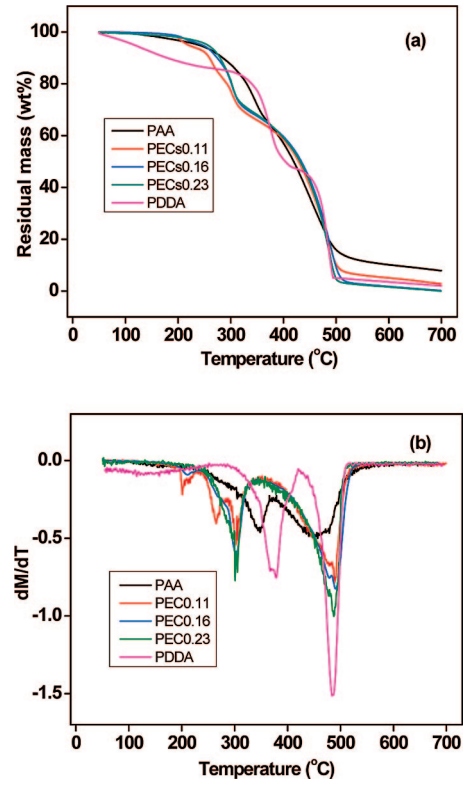


FIGURE 3. Thermal decomposition curves of PEC0.11, PEC0.16, PEC0.23, PAA, and PDDA: (a) TGA; (b) DTA.

between carboxylate and ammonium negatively influenced the strength of the related chemical bond. However, the heat resistance of PECs is generally similar to that of PAA and superior to that of PDDA before 230 °C. The weight loss in the third stage is about 68 wt %, and this is assigned to further decomposition and oxidation of the chars of residue chains.

The glass transition is another important thermal event of polymers, and studies about the glass transitions of PECs are rarely reported. Even among these reports, experimental results are quite different. Huglin et al. (30) reported that a glass transition temperature of PECs between poly[sodium(2-acrylamido-2-methylpropane sulfonate) and poly(4-vinylpyridinium chloride) was not detected because of ionic complexation. There also have been reports that the PECs from ionic intercomponent complexation showed two glass transition temperatures in bulk (31, 32). This naturally leads us to consider that the glass transition temperature of PECs should be dependent on the ICDs of the PECs. However, there have been few studies on how the ICD of a given PEC influences its glass transition temperature. Figure 4 shows the DSC curves of four PECs and PAA, from which it can be seen that the glass transition temperatures of PECs differ greatly from that of PAA. As shown in Figure 4, T_g of PAA is 105 °C and those of PEC0.11 and PEC0.16 are 115 and 123 °C, respectively. Also, it can be clearly seen that the glass transition temperatures of PEC0.11 and PEC0.16 are not as obvious as that of PAA and glass transition temperatures for PEC0.23 and PEC0.39 are undetectable. That is to say, glass transitions of PECs weaken and shift toward higher temperatures simultaneously as the ICD increases and finally

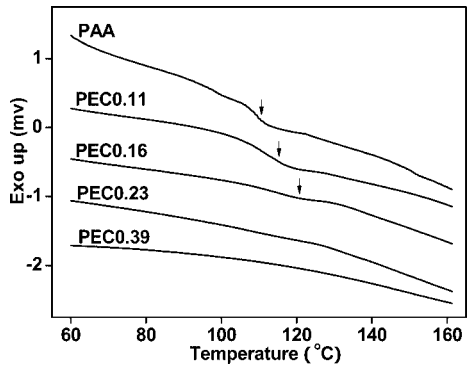


FIGURE 4. DSC curves of PEC0.11, PEC0.16, PEC.23, PEC0.39, and PAA.

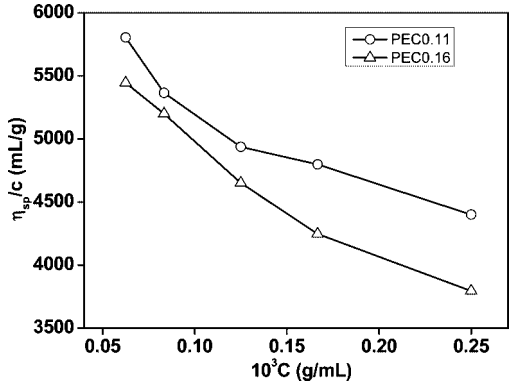


FIGURE 5. $\eta_{sp}/c-c$ curves of PEC0.11 and PEC0.16 in water at 30 °C.

become undetectable. So, this means that the glass transition temperatures of PECs are mainly controlled by the ICD. This is because ionic complexation between PDDA and PAA restricts the mobility of PEC chain segments, because of which the glass transition gradually weakens and finally vanishes when the ICD is above 0.16 in this study.

Viscosity Behavior of PEC Solutions. The viscosity behavior of solid PECs is scarcely studied because of the difficulty in dissolving PECs without breaking the ionic complexation inside it. Figure 5 gives variation of the specific viscosity (η_{sp}/c) with the solution concentration c for PEC0.11 and PEC0.16 in water. It can be seen from Figure 5 that η_{sp}/c values of both PEC0.11 and PEC0.16 increase with decreasing c, showing typical polyelectrolyte behavior, which is mainly due to ionization of carboxylic acid groups in PECs. Furthermore, the η_{sp}/c value of PEC0.16 at the same c is lower than that of PEC0.11; i.e., the $\eta_{sp}/c-c$ line for PEC0.11 is above that for PEC0.16 in the whole concentration range. The ICD of PEC0.16 is larger than that of PEC0.11, and fewer un-ionized carboxylic acid groups remained in the PEC0.16 solid; i.e., there are fewer ionized carboxylic acid groups in PEC0.16 in solution compared with PEC0.11. Thus, the charge density of PEC0.16 is lower in solution and hence has smaller η_{sp}/c values compared with PEC0.11. The other reason is that the restriction of ionic complexation on the expansion of the chains is heavier for PEC0.16 than that for PEC0.11. This restriction in solution is similar to the restriction of ionic complexation on the chain movement in the solid, which results in an increase of T_g with increasing ICD, as shown in Figure 4.

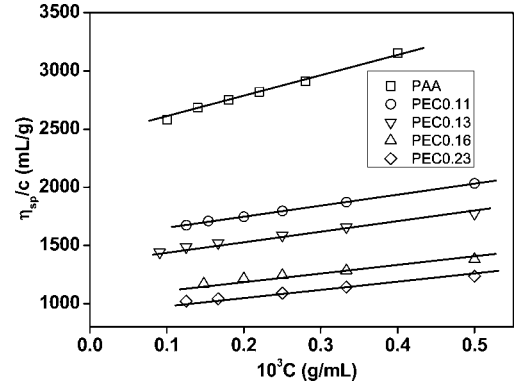


FIGURE 6. $\eta_{sp}/c-c$ curves of PECs and PAA in 0.01 M NaCl at 30 °C.

Table 2. [η] and k_H Values of PECs and PAA in 0.01 M NaCl at 30 °C

sample	[η] (mL/g)	k_H
PAA	2427.3	0.31
PEC0.11	1561.6	0.38
PEC0.13	1385.4	0.42
PEC0.16	1096.6	0.48
PEC0.23	947.6	0.63

Figure 6 shows the $\eta_{sp}/c-c$ curves of four PEC samples and PAA in 0.01 M NaCl at 30 °C. It can be seen from Figure 6 that 0.01 M NaCl can depress the polyelectrolyte behavior of PECs; i.e., the $\eta_{sp}/c-c$ curves of four PECs all show good linearity. Thus, the values of intrinsic viscosities [η] and Huggins constant k_H were obtained by the Huggins equation, and these values were summarized in Table 2. It can be seen from Table 2 that four PECs all have lower [η] and larger k_H than that of PAA. Moreover, [η] decreased and k_H increased with an increase in the ICDs of PECs from 0.11 to 0.23, indicating that both parameters correlate very well with ionic complexation in PECs. It is well-known that [η] and k_H represent the coil dimension or coil density of a polymer in a given solvent and the interaction between the polymer and solvent used, respectively (33, 34). For PECs, the ionic cross-linking restricts the expansion of both chains and decreases the interaction between PECs and water, both of which increase the coil density and result in decreasing [η] and increasing k_H. Because of this, [η] of PECs is lower than that of non-cross-linked PAA and decreases with increasing ICD, and vice versa for k_H of PECs.

Fabrication of HPECMs and Their Performance in Organics Dehydration. Five samples of PEC0.11, PEC0.13, PEC0.16, PEC0.23, and PEC0.29 were all chosen to fabricate HPECMs by the solution-casting method. Figure 7 gives a typical SEM morphology of HPECM0.16. It can be seen from Figure 7 that the surface of HPECM0.16 is glabrous and the cross section is homogeneous at a 20 000× magnification, proving that HPECMs fabricated in this way are homogeneous. HPECMs with five different ICDs were further subjected to dehydration of 10 wt % water−isopropyl alcohol by pervaporation. As shown

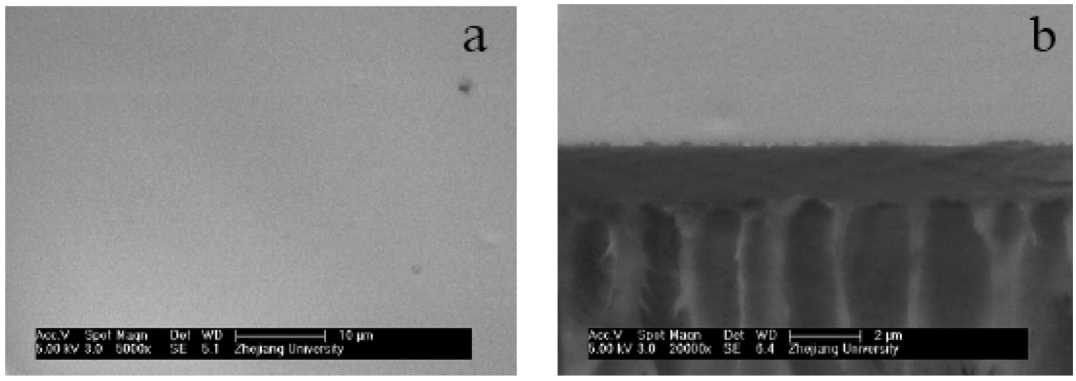


FIGURE 7. SEM micrographs of HPECM0.16: (a) surface; (b) cross section.

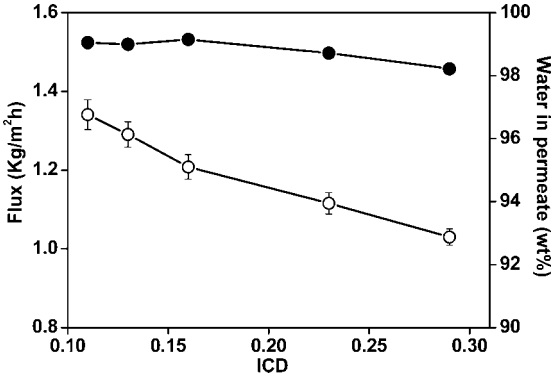


FIGURE 8. Effect of the ICD on the flux (open circles) and water in permeate (solid circles) of HPECMs for dehydration of 10 wt % water−isopropyl alcohol at 40 °C.

in Figure 8, both flux and water in permeate are very high for each HPECM compared with the performance of poly(vinyl alcohol) (35) and other hydrophilic polymeric membranes (36). For example, HPECM0.16 gives a flux of 1.21 kg/m^2 h and 99.15 wt % water in permeate (corresponding to a separation factor of 1049.8) for dehydration of 10 wt % water−isopropyl alcohol at 40 °C. The high flux probably is due to the high hydrophilicity and noncrystalline character of these HPECMs. The high water concentration in permeate is because of the ionic complexation between PAA and PDDA. It also can be seen that the flux gradually decreases as the ICD increases, and this is caused by an increase of the ionic cross-linking degree inside the PECs with increasing ICDs.

Furthermore, another two solution-processable PECs were also fabricated by the same method and subjected to a pervaporation test, and the performances are listed in Table 3. It can be seen from Table 3 that HPECMs made from PDDA-CMCNa and CS-CMCNa PECs all display a very promising performance in the dehydration of 10 wt % water−isopropyl alcohol at 70 °C. The flux is usually the bottleneck of pervaporation, which practically restricted the widespread application of pervaporation. However, all HPECMs in this study surprisingly gave a flux 2 times larger than that of commercially available PERVAP 2510 membrane at the same operation conditions. Moreover, the pervaporation separation index (PSI) of both PDDA-CMCNa and CS-CMCNa HPECMs are far larger than that of the PVAP membrane. In addition, the fluxes of HEPCMs were also far larger than those of their component polyelectrolytes CMCNa and CS. This suggests that HPECMs prepared by the method proposed in this study universally have high performance, especially high flux. The separation mechanism should be interesting, and efforts paid to this topic are ongoing in our laboratory.

CONCLUSIONS

Solution-processable PDDA-PAA PECs were synthesized by protection and deprotection of carboxylic acid groups. Conductance measurement, EA, and the FT-IR spectrum showed that the ICDs of the PECs increased with an increase in the NaOH concentration in both parent polyelectrolyte solutions. The thermal stability of PECs is similar to that of PAA and better than that of PDDA before decomposition. The glass transition of PECs gradually weakens and shifts to higher temperatures with increasing ICD and finally becomes undetectable when ICD is above 0.16. The viscosity property of the PEC diluted solutions displays polyelectrolyte

Table 3. Separation Performances of PDDA-CMCNa and CS-CMCNa HPECMs and Their Component Polyelectrolyte CS and CMCNa Membranes at 70 °C

membrane	permeation flux (kg/m^2 h)	water in permeate (wt %)	separation factor	PSI[a] (kg/m^2 h)
PDDA-CMCNa[b]	2.47	99.15	1049	2591
CS-CMCNa[c]	2.17	99.46	1657	3400
CMCNa	1.10	99.20	1116	1227
CS	0.69	99.41	1516	1046
PERVAP 2510[d]	0.75	98.9	810	607

[a] PSI: pervaporation separation index. [b] PDDA: poly(diallyldimethylammonium cholride). CMCNa: sodium carboxymethyl cellulose. M_{PDDA}:M_{CMCNa} = 0.19. [c] CS: chitosan. M_{CS}:M_{CMCNa} = 0.39. [d] PERVAP 2510: commerical membrane from Sulzer Chemtech GmbH, Linden, Germany. Data for this membrane were from ref 36.

behavior. The [η] of PECs decreases with increasing ICD, and vice versa for the k_H of PECs.

HPECMs of PDDA-PAA PECs were fabricated, whose separation ability was evaluated by pervaporation and found to be excellent. HPECM0.16 gave a performance of $J = 1.21$ kg/m^2 h and $\alpha = 1049.8$ in the dehydration of 10 wt % water−isopropyl alcohol at 40 °C. This high performance is mainly due to the ionic complexation and homogeneity characters of HPECMs. Two other solution-processable PECs, i.e., PDDA-CMCNa and CS-CMCNa PECs, were synthesized by the same method, and their HPECMs also showed very promising separation performances. Thus, this method for the synthesis of solution-processable PECs is applicable for appropriate polyelectrolyte pairs of weak polyanions and strong polycations, and it is expected that the application of PECs as solid materials could be expanded by this method.

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Supporting Information Available: Optical micrographs of a PAA solution at different complexation degrees, detailed EA results of PAA-PDDA PECs, procedure for the synthesis of CS-CMCNa and PDDA-CMCNa PECs, and pervaporation performances of various hydrophilic polymeric membranes in isopropyl alcohol dehydration. This material is available free of charge via the Internet at http://pubs.acs.org.

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