Synthesis and Properties of Amphoteric Copolymer of 5-Vinyltetrazole and Vinylbenzyl Phosphonic Acid

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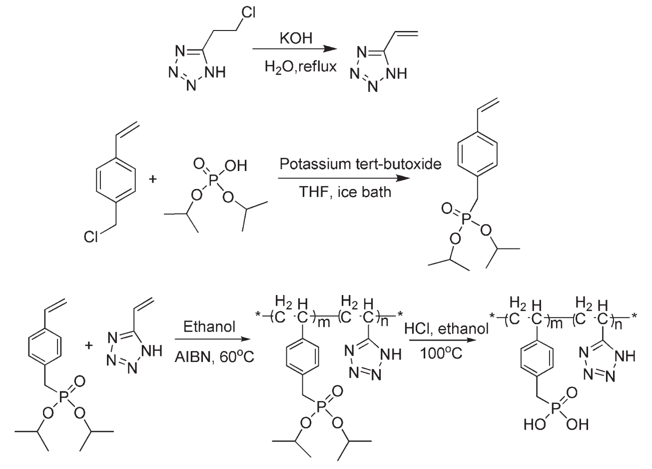
ABSTRACT: Amphoteric polymers have been studied for various applications such as separation of low molecular weight organic molecules from inorganic salt mixtures, selective ion transport, drug delivery through membranes of biological interest, separation of ionic drugs and proteins, and separation of alcohol and water. Typical amphoteric polymers consist of weak base and weak acid groups. In present study, the copolymerization of 5-vinyltetrazole (VT) and diisopropyl-*p*-vinylbenzyl phosphate (DIPVBP) via free radical polymerization is studied. The reactivity ratio of VT and DIPVBP, which is calculated from Kelen-Tudos plot, is 0.251 and 0.345, respectively. The amphoteric copolymer of VT and diisopropyl-p-vinylbenzyl phosphonic acid (poly(VT-*co*-VBPA)) is obtained from hydrolysis of the copolymer of VT and DIPVBP (poly(VT-*co*-DIPVBP)). Poly(VT-*co*-VBPA) is thermally stable under 190 °C. The anhydrous proton conductivity of amphoteric poly(VT-*co*-VBPA) can reach 1.54×10^{-4} S cm^{-1} at 170 °C with an activation energy of 114.7 kJ mol^{-1}. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: amphoteric polymer; conducting polymers; copolymerization; diisopropyl-*p*-vinylbenzyl phosphate; proton conductivity; radical polymerization; 5-vinyltetrazole

INTRODUCTION Among synthetic polyelectrolytes, amphoteric polymers are very close to biological macromolecule in nature and behavior. They may provide useful analogs of proteins and are important to model some properties and functions of biopolymers such as protein folding and enzymatic activity.[1–4] Amphoteric polymers have been studied for various applications such as separation of low molecular weight organic molecules from inorganic salt mixtures,[5–12] selective ion transport,[13–17] drug delivery through membranes of biological interest,[18,19] separation of ionic drugs and proteins,[20,21] and separation of alcohol and water.[22] Amphoteric polymers can comprise chains with combination of weak acid/weak base, strong acid/weak base, (or else weak acid/strong base) and strong acid/strong base monomers. Typical amphoteric polymers consisting of weak base and weak acid groups are copolymers of vinylpyridine and acrylic (or methacrylic) acid. While copolymers of *N*-substituted allyl amine and vinyl sulfonic acids or styrene sulfonic acid belong to strong base/strong acid amphoteric polymers, the acidic and basic groups of amphoteric polymers can also be in salt form with a low or high charge density along the macromolecules.[23]

Proton conducting membrane is a critical part of polymer electrolyte membrane fuel cells (PEMFCs) and determines some critical performance of PEMFCs, such as energy conversion efficiency, longevity. The acid–base interaction in the membranes is very important for the proton transport. Some kinds of water-free acid–base composite membranes have been developed.[24–35] In such kind of systems, acid or base acts as the proton conducting medium. Such as polybenzimidazole (PBI) doped with phosphoric acid, which exhibits good proton conductivity on the order of magnitude 10^{-1} S cm^{-1}, and can work at intermediate temperature (150–200 °C) environment.[26–31] PBI doped with other acids, such as sulfuric acid,[33,34] hydrochloric acid,[33] hydrobromic acid,[34] phosphotungstic acid,[35] silicotungstic acid,[35] were also reported. Some other *N*-heterocycles are also used as the proton transfer medium in polymers.[24,25,36] It is reported that imidazole, benzimidazole, and pyrazole can form hydrogen bonding networks similar to that found in hydrated proton conducting membranes;[37] thus, the proton can be transported via the structure diffusion within acidic and basic moieties. The high proton conductivity can be obtained in these acid–base composite membranes. However, due to high mobility of the small acid or heterocyclic molecules, the softening of the membranes and the leaking of small molecules are also possible. Amphoteric polymers bearing both acidic and basic moieties may exhibit similar anhydrous proton conductivity to acid–base blending membranes.



SCHEME 1 Synthesis of the monomers, and polymerization and hydrolysis of poly(VT-*co*-DIPVBP) to prepare poly(VT-*co*-VBPA).

Vinyl phosphonate can be used as a potential acidic moiety in amphoteric polymers,[38,39] whose ability of polymerization has been reported to be relatively poor.[40] Vinylbenzyl phosphonate was reported more activated.[41–44] Poly(5-vinyltetrazole), a kind of nitrogen-containing heterocyclic polymer, is known to all as one of the thermally stable materials, whose T_d is well above 200 °C and T_g is from 100 to 150 °C depending on the molecular weight. Compared with phosphonic acid, tetrazole moiety exhibits base. It can be prepared either via the method of click chemistry from polyacrylonitrile[45–47] or via the normal free radical polymerization of 5-vinyltetrazole (VT).[48] In this study, diisopropyl-*p*-vinylbenzyl phosphonate (DIPVBP) and VT will be copolymerized, and hydrolyzed to obtain poly(5-vinyltetrazole-*co*-vinylbenzyl phosphonic acid) (poly(VT-*co*-VBPA)). The reactive ratio of these two monomers will be evaluated by the extended Kelen-Tudos (K-T) method. Such kind of amphoteric copolymer may exhibit good proton conductivity under anhydrous condition.

RESULTS AND DISCUSSION

Copolymerization and Reactivity Ratio of VT and DIPVBP

Scheme 1 exhibits the synthesis of the monomers, and polymerization and hydrolysis of poly(VT-*co*-DIPVBP) to prepare poly(VT-*co*-VBPA). Copolymerization of VT and DIPVBP with a series of feed ratios (mol mol^{-1}) according to Table 1 is carried out. The conversion rate is controlled below 10% by reducing the reaction time to calculate the reactivity ratio r_1 and r_2, where 1 and 2 refer to VT and DIPVBP, respectively. The structure of the copolymer is investigated by FTIR spectra (Fig. 1) and ^{1}H NMR (Fig. 2). Figure 1 exhibits the difference of FTIR results between poly(diisopropyl vinylbenzyl phosphate) (PDIPVBP) and poly(vinyltetrazole-*co*-diisopropyl vinylbenzyl phosphate) (poly(VT-*co*-DIPVBP)). Peaks at 2977, 2925 (C—H stretching vibration in isopropyl group), 1176, 1411, and 1105 cm^{-1} (P—O—C stretching vibration) exist in both of the curves, while peaks at 1646, 1152, 1448, 1374 cm^{-1} (characteristic vibration of tetrazole[49,50]) and a broad band between 2250 and 3300 cm^{-1} (N—H stretching vibration) only appear in the curve of sample **3**. In Figure 2, all the signals appeared agree well with the expected structure, except the signal of N—H in tetrazole. Combining the results

TABLE 1 Condition and Yield of the Copolymerization of VT and DIPVBP at 60 °C

Samples	[M$_1$]:[M$_2$] (mol mol^{-1})	Reaction Time (h)	([M$_1$]+[M$_2$]): AIBN	Conversion Ratio (%)
1	90:10	1	100:1	8.2
2	70:30	1	100:1	8.0
3	50:50	3	100:1	6.1
4	30:70	3	100:1	5.8
5	10:90	3	100:1	5.2

M$_1$: VT; M$_2$: DIPVBP.

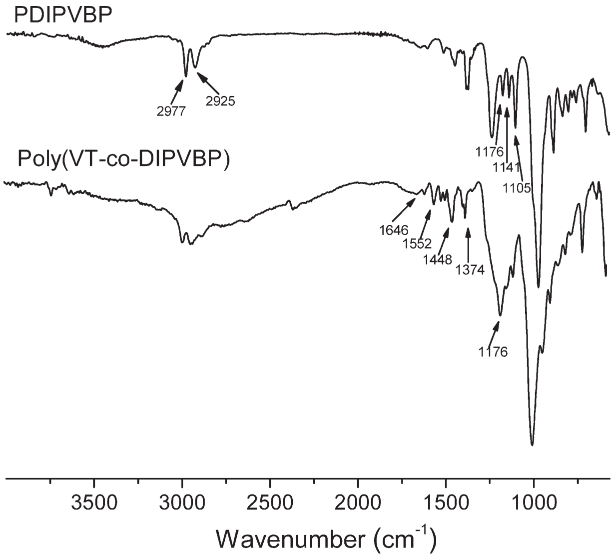


FIGURE 1 FTIR spectra of PDIPVBP and poly(VT-*co*-DIPVBP) (sample **3**).

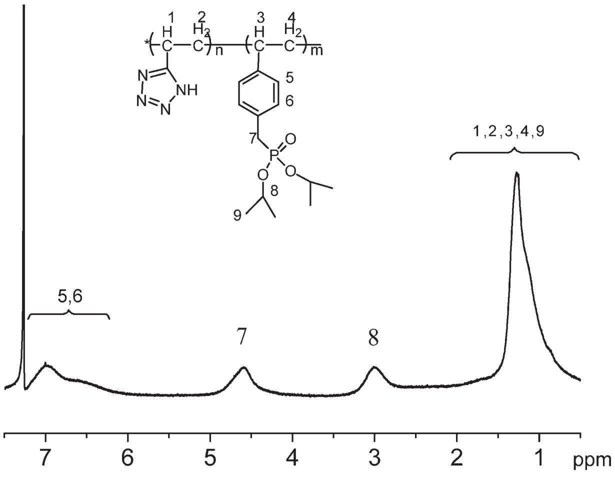


FIGURE 2 ^{1}H NMR of poly(VT-*co*-DIPVBP) (sample **3**) in CDCl$_3$.

TABLE 2 Feed Ratio of VT and DIPVBP and the Actual Composition in Poly(VT-*co*-DIPVBP)

		Element Content Measured					
Samples	$[M_1]$:$[M_2]$ (mol:mol)	C (%)	H (%)	N (%)	F_{1e} (%)	F_1c (%)	δ^a (%)
1	90:10	44.96	6.49	27.30	76.20	75.83	−0.48
2	70:30	53.08	7.98	18.06	58.33	58.00	−0.55
3	50:50	55.35	7.80	13.39	47.94	48.19	0.52
4	30:70	58.69	8.12	8.79	34.76	38.03	9.39
5	10:90	60.00	7.98	5.27	23.03	20.03	−13.05

M_1: VT; M_2: DIPVBP; F_{1e}: instantaneous molar ratio of M_1 in the copolymers obtained by experiment. F_1c: instantaneous molar ratio of M_1 in the copolymers obtained by the calculation from eq 2 with r_1 = 0.251 and r_2 = 0.345.

[a] $\delta = (F_1\text{c} - F_1\text{e})/F_1\text{e}$.

of FTIR with ^{1}H NMR spectra, the expected structure of poly(VT-*co*-DIPVBP) can be confirmed.

The actual composition of the copolymers is calculated from the results of elemental analysis, and summarized in Table 2. According to Table 2, the composition curve of the copolymers, which can roughly describe the copolymerization behavior of two monomers, is plotted in Figure 3. It is indicated that this copolymerization is the nonideal copolymerization with a constant proportion point, where both r_1 and r_2 are below 1. The reactivity ratio between two monomers is calculated by using K-T Equation,[51] which can be applied in a steady state, where the conversion ratio is below 10%. K-T Equation is shown in eq 1:

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right]\xi - \frac{r_2}{\alpha} \tag{1}$$

where $\eta = \frac{G}{\alpha + H}$, $\xi = \frac{H}{\alpha + H}$, $\alpha = \sqrt{H\text{min} \times H\text{max}}$, $G = R(\rho - 1)/\rho$, $H = R^2/\rho$, $R = [M_1]/[M_2]$, $\rho = d[M_1]/d[M_2]$. The results calculated by K-T Equation are shown in Table 3. The reactivity ratio is obtained from K-T plot of ξ and η, as shown in Figure 4. It was shown that the determinants of coefficient (R^2) of the fitted straight line is 91.50%, and the reactivity ratio (r_1 and r_2) of VT and DIPVBP is 0.251 and 0.345 by calculation, respectively, which means both of them incline to copolymerize with each other.

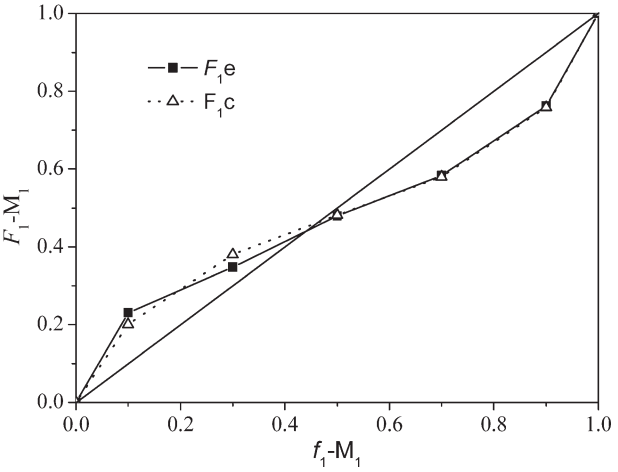


FIGURE 3 *F*–*f* curve of VT in the copolymerization of VT and DIPVBP.

To estimate the accuracy of the reactivity ratio, a calculated result of the instantaneous mole fraction of M1 in the copolymer (F_1c) is obtained from eq 2 with the obtained reactivity ratio for fitting. The results of F_1c are listed in Table 2, and δ is to represent the difference between F_1e (instantaneous mole fraction of M1 in the copolymer which was obtained by experiment) and F_1c. The fitting curve of F_1c–f_1 is exhibited in Figure 3. It can be seen from Table 2 that δ is less than 0.55% for samples 1–3, which is a little higher than that for samples 4 and 5. However, the F_1c–f_1 curve fits very well with F_1e–f_1 curve, which demonstrates that the obtained reactivity ratios are reliable:

$$F_1c = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}. \tag{2}$$

Hydrolysis of Poly(VT-*co*-DIPVBP)

Poly(VT-*co*-VBPA) is prepared from the hydrolysis of poly(VT-*co*-DIPVBP) in HCl/ethanol solution for 24 h. In Figure 5, peaks at 3382 cm^{-1} (PO—H) and 929 cm^{-1} (P—OH) on the curve of poly(VT-*co*-VBPA) indicate that poly(VT-*co*-DIPVBP) has been hydrolyzed successfully. While peaks at 2989 cm^{-1} and 2925 cm^{-1} (C—H stretching vibration in isopropyl group) indicate that the hydrolysis is incomplete.

Molecular Weight and Thermal Properties of the Copolymers

The molecular weight and polydispersity index of the polymers are determined by GPC and listed in Table 4. The glass transition temperature (T_g) of the copolymer is determined by half Cp extrapolated temperature in DSC, as shown in Figure 6. The typical glass transition temperature of poly(VT-*co*-DIPVBP) is 141.6 °C, while that of corresponding poly(VT-*co*-VBPA), which is obtained from the hydrolysis of poly(VT-*co*-DIPVBP), is 152.3 °C. After hydrolysis, the heat capacity difference (ΔC_p) is lowered from 0.607 to 0.376 J

TABLE 3 Data of Relative Parameters for Kelen-Tudos Method

	Feed Composition		Copolymer Composition					
Sample	$[M_1]$ (mol %)	R	$d[M_1]$ (mol %)	ρ	G	H	ξ	η
1	90	9	76.20	3.20	6.19	25.30	0.96	0.24
2	70	2.33	58.33	1.40	0.67	3.89	0.79	0.14
3	50	1	47.94	0.92	−0.09	1.09	0.52	−0.04
4	30	0.43	34.76	0.53	−0.38	0.35	0.26	−0.28
5	10	0.11	23.03	0.30	−0.26	0.04	0.04	−0.25

$\alpha = \sqrt{H\min \times H\max} = 1.006$.

$g^{-1}\cdot{}^{\circ}C^{-1}$, T_g is improved and the region of the glass transition temperature of poly(VT-*co*-VBPA) becomes wider. These can be attributed to the enhancement of intermolecular and intramolecular interaction. After the hydrolysis, phosphonic acid groups formed are prone to forming hydrogen bonds with each other or with tetrazole groups, which restricts the segmental motion.

TGA analysis is performed under nitrogen atmosphere, as shown in Figure 7. The slight weight loss in the curve of sample **3** before 150 °C may be attributed to the loss of physically bonded water. Compared with sample **3**, the curve of poly(VT-*co*-VBPA) has a weight loss before 200 °C, which can be attributed to the dehydration reaction between phosphonic acid groups. Both of them degrade drastically at 190 °C, which can be attributed to the degradation of tetrazole, while PDIPVBP is reported to be degraded at 250 °C.[16,17]

Proton Conductivity of Poly(VT-*co*-VBPA)

Tetrazole is a group which has proton transfer properties similar to that of imidazole or water. Tetrazole commonly exists in two tautomeric forms, 1H-tetrazole and 2H-tetrazole.[52–54] The equilibrium between these two forms relates to the morphology and solvents.[54–63] Transformation of two forms of tetrazoles provides the possibility for the transport of protons. In fact, tetrazole itself is an amphoteric molecule with p*K*a ≈ 5.[64–66] However, compared with phosphonic acid, tetrazole moiety exhibits basic, which is the proton acceptor. The interaction between tetrazole and phosphonic acid moieties in poly(VT-*co*-VBPA) may provide improved anhydrous proton conductivity.

The proton conductivity of poly(VT-*co*-VBPA) membranes is determined under intermediate temperature (100–170 °C) environment. The test cell is first heated to 180 °C and held 10 min to eliminate any impact of humidity. Then the conductivities of the membranes are measured during the cooling process. Figure 8 shows that the proton conductivity increases with increasing temperature. The ratio between phosphonic acid and tetrazole groups has dominant influence on proton conductivity. The highest anhydrous proton conductivity obtained in sample **5** at 170 °C can reach 1.54×10^{-4} S cm^{-1}. In these membranes, both tetrazole and phosphonic acid can act as proton donor or acceptor. Thus, the proton-transferring channels may form in the membranes.

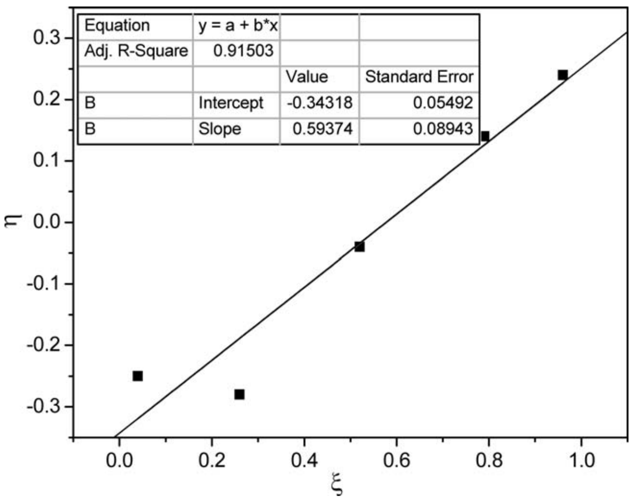


FIGURE 4 Kelen-Tudos plot for the copolymerization of VT and DIPVBP.

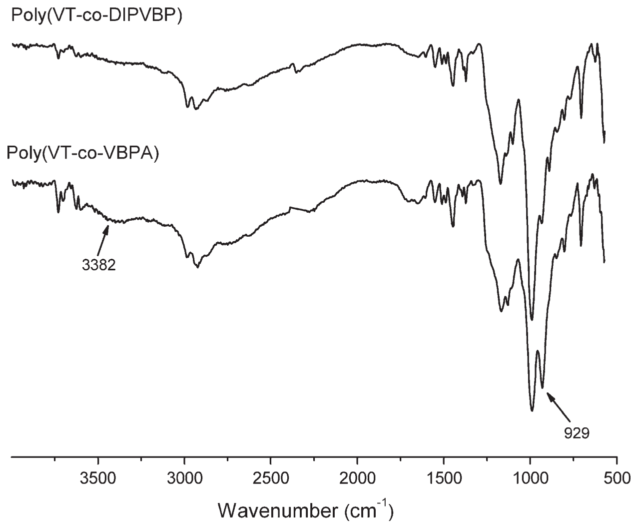


FIGURE 5 FTIR spectra of poly(VT-*co*-DIPVBP) (sample **3**) and corresponding poly(VT-*co*-VBPA).

TABLE 4 Number Average Molecular Weight (M_n) and Polydispersity Index of the Polymers

Samples	1	2	3	4	5
M_n (10^3 Dalton)	42.6	27.0	17.0	29.1	29.0
Polydispersity index	1.88	1.71	1.53	1.54	1.47

The proton conduction mechanism of poly(VT-*co*-VBPA) can be better understood from Arrhenius plot of conductivity (eq. 3),[31,67]

$$\sigma = \sigma_0 \exp\left(-\frac{E_\alpha}{RT}\right) \tag{3}$$

where σ_0 is a pre-exponential factor, E_a is the activation energy, R is Boltzman constant, and T is the temperature. The temperature dependence of the proton conductivity of poly(VT-*co*-VBPA) fits well with a simple Arrhenius equation as shown in Figure 8, which indicates that the hopping mechanism is preferred for the proton conductivity.

Through the comparison between the tetrazole-dominant sample **1** and VBPA-dominant sample **5**, it is shown that the proton transfers easier and faster between phosphoric acid than between tetrazoles, as the activation energy of sample **5** is as low as 114.7 kJ mol^{-1} while that of sample **1** has the highest value 219.4 kJ mol^{-1} among these polymers. Besides, the highest anhydrous proton conductivity is obtained by sample **5** at 170 °C which reaches 1.54×10^{-4} S cm^{-1}. The high proton conductivity of sample **5** can be attributed to the low activation energy and abundant active protons as one VBPA unit possess two active protons but one tetrazole unit contains only one.

When more tetrazoles and phosphoric acids participate in the proton transfer, the situation becomes complicated. The interaction between VBPA unit and tetrazole shows negative influence on the proton conductivity by restricting the segmental motion. One tetrazole contains four nitrogen sites might tend to interact with two VBPA units by acid–base interaction or electrostatic interaction. The interaction between VBPA and tetrazole will be the strongest when the molar ratio of which is 2:1. Therefore, sample **4** (VBPA: tetrazole = 7:3, the molar ratio of which is about 2:1) has stronger interaction in the polymer and exhibits lower proton conductivity and higher activation energy than sample **2** and sample **3**. The anhydrous proton conductivity of poly(VT-*co*-VBPA) is comparable to other reported amphoteric polymers. Such as poly(EGMAP-*co*-4-VIm) exhibited conductivity of 10^{-6} to 10^{-10} S cm^{-1} at 30–150 °C,[38] poly(VPA-*co*-4-VIm) showed 10^{-6} to 10^{-12} S cm^{-1}.[39]

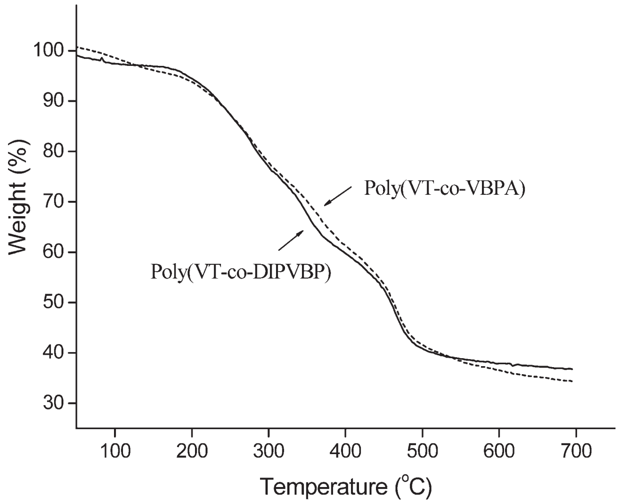


FIGURE 7 TGA results of poly(VT-*co*-DIPVBP) (sample **3**) and corresponding poly(VT-*co*-VBPA).

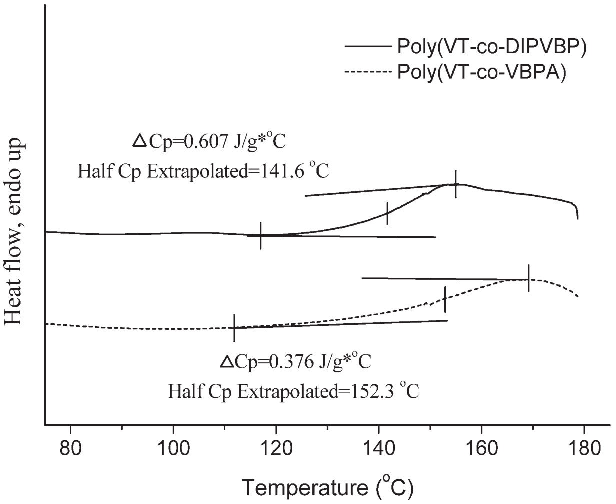


FIGURE 6 DSC results of poly(VT-*co*-DIPVBP) (sample **3**) and corresponding poly(VT-*co*-VBPA), heating rate 10 K min^{-1}.

Scheme 2 exhibits the possible proton transport in poly(VT-*co*-VBPA) membranes by hopping mechanism. As tetrazole has four nitrogen atoms, which can form hydrogen bonds on

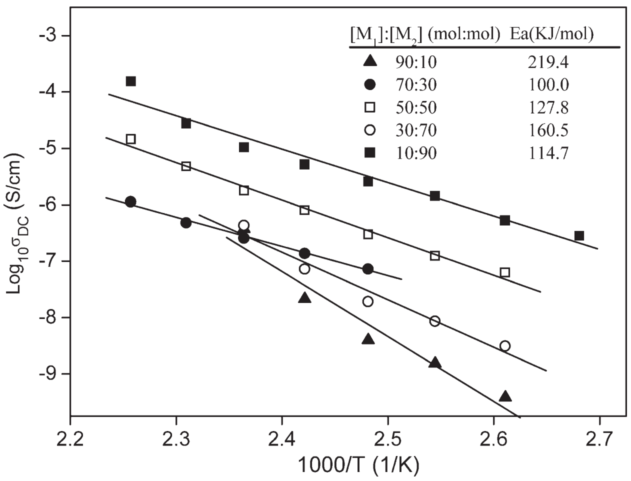
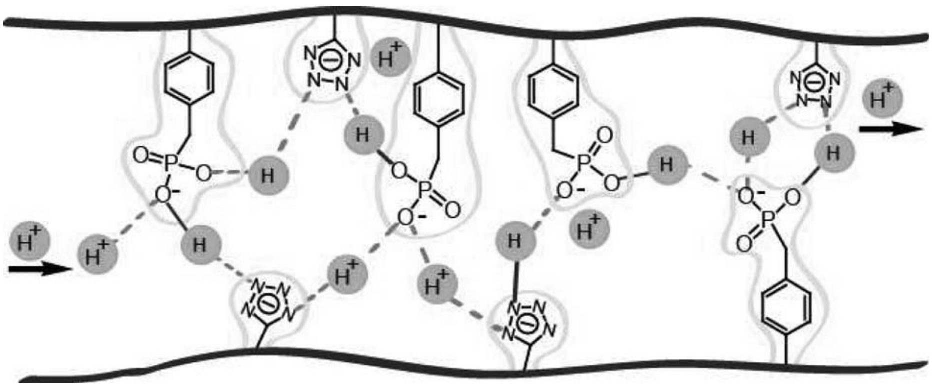


FIGURE 8 Temperature dependence of the proton conductivity and the activation energy of poly(VT-*co*-VBPA).



SCHEME 2 Proton hopping mechanism in the membranes.

every site of tetrazole ring.[68,69] Hydrogen bonds are easy to form between phosphonic acid and tetrazole groups. Therefore, the network of the hydrogen bonds is easy to be formed in the membranes. The protons are hopping through the forming and breaking of the hydrogen bonds from one end to the other, as described in Scheme 2. The proton transport in the membrane is thus achieved.

EXPERIMENTAL

Materials

Diisopropyl phosphate (98%, Alfa Aesar), *p*-vinylbenzyl chloride (97%, Aldrich), potassium *tert*-butoxide (98%, Acros Organics), 5-(2-chloroethyl)tetrazole (95%, Nantong Huafeng Chemical) were all used as received. Azobisisobutyronitrile (AIBN, 95%) from Shanghai Chemical Reagent was recrystallized from alcohol before use. Tetrahydrofuran (THF) from Shanghai Chemical Reagent was dried over sodium.

Synthesis of DIPVBP

DIPVBP was synthesized according to the method similar to that in literature.[16,17,70] The solution of diisopropyl phosphate (14.19 g, 85.4 mmol) and *p*-vinylbenzyl chloride (10.72 g, 70.25 mmol) in dry THF (20 mL) was placed in a flask and stirred in ice bath, then potassium *tert*-butoxide (8.16 g, 72.7 mmol) in dry THF (40 mL) was added dropwise within 2 h. The reaction was maintained for another hour, and then filtered, diluted in diethyl ether (200 mL), and washed with water for three times. The organic component was dried over sodium sulfate, and purified by silica gel column chromatography (yield = 60%).

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.18 (4H, Ar-H), 6.70 (1H, $CH{=}CH_2$), 5.70 (1H, $CH{=}CH_2$), 5.20 (1H, $CH{=}CH_2$), 4.60 (2H, $CH(CH_3)_2$), 3.11 (2H, $CH_2{-}P$), 1.11 (12H, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.3 (CH_3), 33.0 ($\underline{C}H_2{-}P$), 62.0 (d, $CH_2{-}O$, ^2J = 6.90 Hz), 113.5 ($CH{=}CH_2$), 126.2 ($\underline{C}H{=}CH_2$), 130.0 (d, $\underline{A}$r-H, ^2J = 6.69 Hz), 131.5 (d, $\underline{A}$r-CH_2, ^2J = 9.40 Hz), 136.0 ($\underline{A}$r-H), 136.4($\underline{A}$r-H).

Synthesis of VT

VT was synthesized according to the method similar to that in references.[50,71] 5-(2-chloroethyl) tetrazole (2 g, 15 mmol), KOH (3 g, 54 mmol), deionized water (15 mL), and hydroquinone (5 mg, 0.045 mmol) were placed in a flask. The solution was stirred at 80 °C for 2.5 h. Then after cooled down to room temperature, the pH value of the solution was adjusted to 2 or 3 by adding the concentrated hydrochloric acid. The product was extracted by ethyl acetate, and filtered. The yellowish crude product was obtained after ethyl acetate being distilled in vacuum. Then the crude product was recrystallized in chloroform (yield= 65%).

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.90 (1H, $CH{=}CH_2$), 6.50 (1H, $CH{=}CH_2$), 5.90 (1H, $CH{=}CH_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 119.59 ($\underline{C}H{=}CH_2$), 125.20 ($\underline{C}H_2{=}CH$), 154.4 ($\underline{C}{-}CH{=}CH_2$).

Synthesis of Poly(5-vinyltetrazole-*co*-vinylbenzyl phosphonic acid) and PDIPVBP

The copolymerization of VT with DIPVBP was carried out in ethanol at 60 °C under nitrogen atmosphere with AIBN as the initiator. The feed ratio of VT, DIPVBP, and other additives are summarized in Table 1. After a certain time of polymerization, the solution was poured into excess hexane to precipitate out the copolymer. The copolymer was washed several times by hexane and dried under vacuum at 60 °C for 48 h. The composition of poly(VT-*co*-DIPVBP) synthesized was determined by elemental analysis, ^{1}H NMR, and FTIR spectra. Poly(VT-*co*-DIPVBP) was then dissolved in ethanol and reacted with excess concentrated HCl solution at 100 °C for 24 h, and the corresponding product of the hydrolysis, poly(vinyl tetrazole-*co*-vinylbenzyl phosphonic acid), was obtained after purification.

For comparison, PDIPVBP was prepared by the polymerization of DIPVBP. A polymerization tube was charged with 0.282 g DIPVBP (1 mmol), 2.4 mg AIBN, and 10 mL ethanol. Then the tube was bubbled by N_2 for 10 min and sealed. The reaction was held at 60 °C for 24 h, after which the solution was poured into 100 mL hexane. The precipitate was filtered and dried in vacuum.

Characterization

FTIR spectra of the copolymers were measured on EQUINOXSS/HYPERION 2000 (Bruker). ^{1}H NMR and ^{13}C NMR spectra of the samples were measured on Bruker AC 250 spectrometer. Elemental analysis of the copolymers was measured on Elementar Vario EL III. Thermogravimetric analysis (TGA) of the copolymers was measured on STA 499C (Netzsch) with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. DSC measurements were carried out on DSC Q100 (TA) under nitrogen atmosphere from room temperature to 180 °C, with a heating rate of 10 °C min^{-1}.

Gel permeation chromatography (GPC) measurements were carried out on a Waters GPC e2695 instrument with three column set (Styragel HR3 + HR4 + HR5) equipped with refractive index detector (Waters 2414), and DMF (containing 1 g L^{-1} LiBr) as eluent at 45 °C. The calibration was performed with poly(methyl methacrylate) standards in the range of $M_p = 2580$ to 981,000 (Polymer Standards Service-USA).

The proton conductivity of the polymers was measured on Electrochemical Impedance Laboratory CHI 604B (CH Instruments). The proton conductivity σ can be calculated by using the equation $\sigma = L/RA$, where L and A are the thickness of the samples and the contact area between the electrode and the membrane, respectively. While the impedance R can be obtained from Cole–Cole plot of the impedance diagram. In these experiments, polymer membranes with thickness of 30–50 μm were sandwiched between two round electrodes. The samples were heated to 180 °C and held for 10 min. Then the conductivities were measured during the cooling process.

CONCLUSIONS

A series of poly(VT-*co*-DIPVBP) are synthesized via free radical copolymerization. The reactivity ratio of VT and DIPVBP is 0.251 and 0.345, respectively. Poly(VT-*co*-VBPA) can be obtained from the hydrolysis of poly(VT-*co*-DIPVBP). The copolymers are thermally stable under 190 °C. The anhydrous proton conductivity of poly(VT-*co*-VBPA) can reach 1.54×10^{-4} S cm^{-1} at 170 °C, which makes them great promising for proton conducting materials in intermediate temperature PEMFCs.

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