Proton-Conducting Polymers via Free Radical Polymerization of Diisopropyl-*p*-vinylbenzyl Phosphonate and 1-Vinylimidazole

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ABSTRACT: Copolymers of diisopropyl-*p*-vinylbenzyl phosphonate (DIPVBP) and 1-vinylimidazole (1VI) prepared by free radical polymerization were studied. It was found that 1-vinylimidazole can be polymerized with DIPVBP. The reactivity ratios of 1VI and DIPVBP obtained from Kelen−Tudos plots were 0.10 (r_1: 1VI) and 3.10 (r_2: DIPVBP), respectively. According to the reactivity ratios, it is presumed that the imidazole moiety is surrounded by the phosphonate groups in the early stage of the copolymerization. A proton-conducting copolymer of vinylbenzylphosphonic acid and 1-vinylimidazole (P(VBPA-*co*-1VI)) was then obtained from poly(diisopropyl-*p*-vinylbenzyl phosphonate-*co*-1-vinylimidazole) by hydrolysis of the phosphonate groups, which exhibits higher proton conductivity (10^{-1} S cm^{-1} at 30 °C) than the homopolymer of poly(vinylbenzylphosphonic acid).

Introduction

Proton-conducting polymers with a variety of properties have been the focus of polymer research for many years due to the possibility of their application in various electrochemical devices.[1−3] The phosphonic acid-based polymer has recently attracted much attention in the field of proton conductivity. However, phosphonic acid groups grafted onto the polymer main chains used as alternative ion exchange groups have not been widely investigated due to the difficulty to produce C−P bonds.[4−7]

Up until now, vinyl-based phosphonic acid is almost the only monomer containing a phosphonic acid group which is focused on. Poly(vinyl phosphonic acid) can be prepared by the hydrolysis of the corresponding vinyl phosphonate-based polymers. However, the ability of homopolymerization or copolymerization of vinyl phosphonates by free radical initiator has been reported to be relatively poor.[8,9] The low molecular weight compound obtained results from the chain transfer to the alkoxy groups linked to the phosphorus atom of the monomer or polymer.[10] Several solutions have been proposed, especially the use of different techniques of polymerization,[2,11] finding adequate comonomers,[12] and the activation of the double bond by introducing a polarizing substitution group R_1, such as C_6H_5, CN, COOR, or OCOR groups, according to the following general formula: $H_2C{=}CR_1P(O)(OR)_2$, with R = alkyl or halogenoalkyl.[13]

Recently, the composite based on N-heterocyclic polymer and acid as anhydrous proton-conducting materials are widely studied, in which N-heterocycles may act as proton acceptor compared with the acidic moiety.[14−17] Copolymerization of N-heterocyclic monomers with diisopropyl-*p*-vinylbenzyl phosphonate (DIPVBP) and hydrolysis thereafter to form vinylbenzylphosphonic acid-based copolymer may be a good approach for the development of novel proton-conducting polymers with both proton donor and proton acceptor.

Among several procedures available to determine reactivity ratios of the monomers, the methods of Mayo−Lewis,[18] Finemann−Ross,[19] inverted Finemann−Ross,[20] Kelen−Tudos (K−T),[21] Tidwell−Mortimer,[22] and Mao−Huglin[23] are extensively used. The K−T method is a linear least-squares (LLS) method that can be applied at low conversions (<10%). In the present work, a new copolymer was synthesized by free-radical copolymerization of DIPVBP with 1-vinylimidazole (1VI). As the copolymerization of DIPVBP and 1VI at the early stage follows the simple terminal model of copolymerization, the reactivity ratios of the monomers can be evaluated by the extended K−T method using the results of elementary analysis of the copolymer composition obtained at a wide range of monomer feed ratios. And then the proton-conducting copolymer, poly(vinylbenzylphosphonic acid-*co*-1-vinylimidazole) (poly(VBPA-*co*-1VI)) with different composition, was obtained by the hydrolysis of the phosphonate groups.

Experimental Section

Materials. 1VI (99%, Aldrich) was distilled twice under reduced pressure. AIBN was recrystallized from methanol prior to use. Tetrahydrofuran (THF, Shanghai Chemical Reagent Co.) was dried over phosphorus pentoxide prior to use. Vinylbenzyl chloride (97%, Aldrich), diisopropyl phosphate (98%, Alfa Aesar), potassium *tert*-butoxide (97%, Aldrich), and the other chemicals were all used as received.

Synthesis of DIPVBP. Diisopropyl-*p*-vinylbenzyl phosphonate was synthesized in a similar method adapted from the literature.[24] Potassium *tert*-butoxide (8.16 g, 72.7 mmol) in dry THF (40 mL) was then added dropwise into stirred solution of diisopropyl phosphate (14.19 g, 85.4 mmol) and *p*-vinylbenzyl chloride (10.72 g, 70.25 mmol) in THF within 2 h. And the reaction was maintained at room temperature throughout by occasional cooling with an ice bath. The mixture was kept stirring for another hour at room temperature and then filtered, diluted with diethyl ether (200 mL), and washed with water (100 mL) three times. The organic component was then dried over sodium sulfate. The raw product was then purified by flash column chromatography on silica. Residual vinylbenzyl chloride was eluted with toluene, and subsequently the product was washed off with ethyl acetate to yield colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.08 (4H, Ar−H), 6.48 (1H, C*H*=CH_2), 5.36 (1H, CH=C*H*$_2$), 5.02 (1H, CH=CH_2), 4.40 (2H, C*H*$(CH_3)_2$), 2.91 (2H, CH_2−P), 1.11 (12H, CH_3).

Synthesis of Poly(diisopropyl-*p*-vinylbenzyl phosphonate-*co*-1-vinylimidazole). The synthesis of the copolymers with various feed ratios of 1VI and DIPVBP was carried out in toluene solution at 70 °C with AIBN as initiator. The copolymers (the feed ratios of monomers and other materials are summarized in Table 1) were synthesized by dissolving 1VI and DIPVBP in toluene. AIBN in toluene was added into the solution. The reaction mixture was stirred under a nitrogen atmosphere for a certain time, which is shown in Table 1. The reaction mixture of polymerization, which was transparent, was poured into excess hexane to precipitate out the copolymers and then washed with hexane several times. The

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Table 1. Condition and Yield of the Copolymerization[a]

samples	DIPVBP:1VI (feed ratio, mol/mol)	$[M]_0$:[AIBN]:[toluene]	reaction time (h)	yield (%)
1	10:90	100:1:1000	1.2	8.4
2	30:70	100:1:1000	1.1	8.1
3	50:50	100:1:1000	1	8.8
4	70:30	100:1:1000	1	8.9
5	90:10	100:1:1000	1	9.1
6	90:10	100:10:1000	0.5	7.44
7	90:10	100:0.1:1000	2	7.14

[a] The reaction temperature is 70 °C.

copolymers were dried under vacuum at 70 °C for 48 h, and the composition of the copolymers was determined by elementary analysis.

The homopolymers of DIPVBP and 1VI were synthesized by free radical polymerization in toluene with the similar condition to the copolymers. The reaction mixture of the polymerization of DIPVBP, which was transparent, was poured into excess hexane to precipitate out poly(diisopropyl-*p*-vinylbenzyl phosphonate) (PDIPVBP). 1VI can be dissolved in toluene, while poly(1-vinylimidazole) (P1VI) will precipitate from toluene and can be filtrated. As the reaction ratio is high, a yield ratio as high as 60% still can be available.

Preparation of Poly(vinylbenzylphosphonic acid-*co*-1-vinylimidazole). Poly(diisopropyl-*p*-vinylbenzyl phosphonate-*co*-1-vinylimidazole) prepared above was dissolved in ethanol and reacted with excess HCl aqueous solution (10 mol/L) at 100 °C for 24 h, and the corresponding poly(vinylbenzylphosphonic acid-*co*-1-vinylimidazole) was obtained after purification.

Characterization. Infrared spectra of the membranes were measured in transmission mode with a EQUINOXSS/HYPERION2000. ^{1}H NMR spectra of the samples were recorded with a Bruker AC 250 spectrometer in $CDCl_3$. Elementary analysis of copolymers was measured with Elementar Vario EL III. Thermogravimetric analysis (TGA) of the copolymers was investigated with STA 449 C (Netz Co.). The samples were heated with a rate of 10 °C/min from room temperature to 1000 °C under an air atmosphere. DSC measurements were carried out between −80 and 200 °C using a DSC Q100 V9.4 Build 287, heating rate 10 °C/min. Molecular weights of the copolymers were measured by a Waters GPC with THF as solvent.

The proton conductivity of membranes was measured by ac impedance spectroscopy, a system based on a model Electrochemical Impedance Laboratory CHI 604B (CH Instruments Inc.), which worked in the galvanostatic mode and produced a proton current across the membrane. The membrane was placed between two gold-coated electrodes, and the direction of conductive measurement is perpendicular to the membrane. The conductivity of the sample was obtained from complex impedance analysis. The real and imaginary parts of the complex impedance were plotted, and the proton conductivity was obtained from the bulk resistance found in complex impedance diagram. The proton conductivity can be calculated by using the equation $\sigma = L/RA$, where L and A are the thickness of the sample and the contact area between the electrode and the membrane, respectively. R is the resistance from the impedance data.

Results and Discussion

Reactivity Ratios of Diisopropyl-*p*-vinylbenzyl Phosphonate and 1-Vinylimidazole. Poly(diisopropyl-*p*-vinylbenzyl phosphonate-*co*-1-vinylimidazole) (poly(DIPVBP-*co*-1VI)) was synthesized with feed ratio (mol/mol) of 1VI/DIPVBP ranging from 90/10 to 10/90. The conditions and the results of the copolymerization are summarized in Table 1. In order to obtain the reactivity ratios r_1 and r_2 (1 and 2 refer to 1VI and DIPVBP, respectively), the yields were controlled under 10% by reducing the reaction time.

No precipitate formed during the reactions, and the solution remained transparent except sample 1 in Table 1. The copolymers, which were obtained at higher feed ratios of 1VI, can be partially swollen in water. As the feed content of DIPVBP increases, the resultant copolymers become insoluble in water, which may be due to the interpolymer complexation.

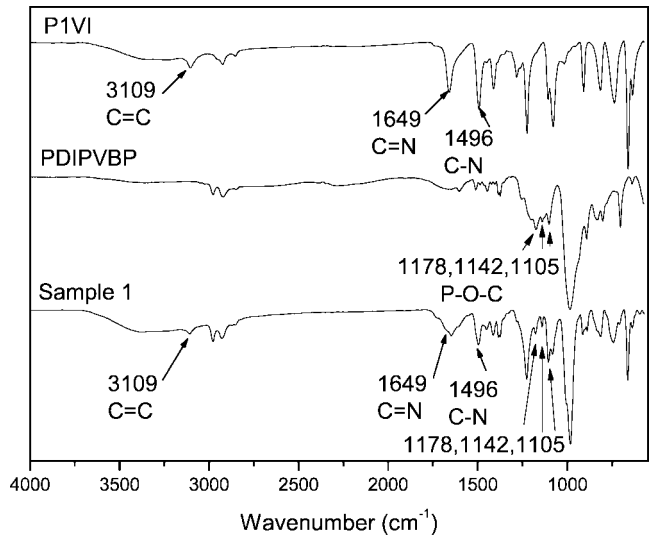

Figure 1. Infrared spectra of P1VI, PDIPVBP, and poly(DIPVBP-*co*-1VI) (sample 1).

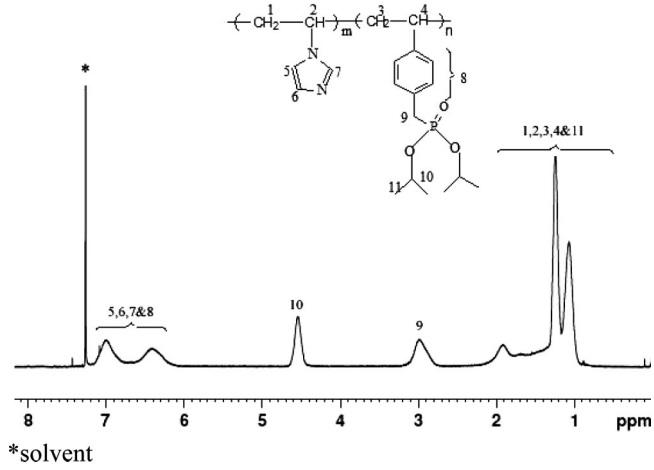

Figure 2. ^{1}H NMR spectra of poly(DIPVBP-*co*-1VI) (sample 3), with $CDCl_3$ as solvent.

The structure and composition of the copolymer were investigated by FTIR spectra (Figure 1) and ^{1}H NMR spectra (Figure 2). As it is shown in Figure 1, the copolymers synthesized in this paper contain the characteristic groups which exist in the imidazole ring (3109 cm^{-1}, C=C; 1649 cm^{-1}, C=N; 1496 cm^{-1}, C−N) of P1VI and phosphonate group (1178, 1142, 1105 cm^{-1}, P−O−C) of PDIPVBP, respectively. The spectrum of PDIPVBP has a band at 3435 cm^{-1}, attributed to free hydroxyl groups. The center of the hydrogen-bonded hydroxyl band is shifted to 3402 cm^{-1} in the spectrum of the copolymer (sample 1). As the VI content in the copolymer increases, the intensity of free hydroxyl band decreases. At the same time, the center band of the broad hydrogen-bonded hydroxyl shifts to a lower frequency (3365 cm^{-1}) in P1VI. The results suggest that hydrogen bonds can be formed easily in the copolymers with the imidazole ring in the main chain.

In ^{1}H NMR spectra of the copolymer, around 6.5 and 7.4 ppm, two signals appear which can be assigned to imidazole ring and benzene ring protons. Signals corresponding to backbone protons appear between 1.0 and 2.0 ppm. According to ^{1}H NMR spectra of the two monomers[24] and the copolymer

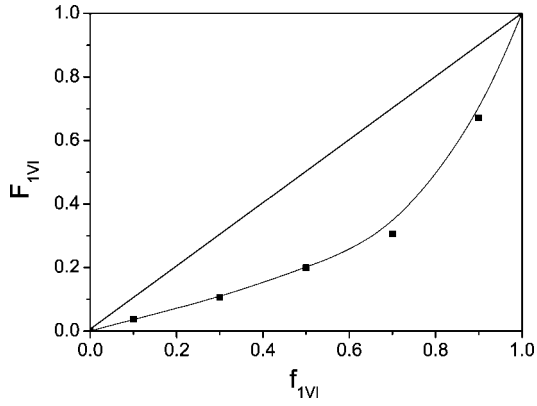

Figure 3. $F-f$ curve of 1VI in the copolymer.

Table 2. Feed Ratio of Monomers and the Actual Composition in the Copolymers

sample	DIPVBP:1VI (feed ratio, mol/mol)	actual composition in the copolymers measured by elementary analysis (mol %) C (%)	H (%)	N (%)	mol % of 1VI in the copolymers
1	10:90	57.37	5.96	10.72	67.1
2	30:70	59.95	6.26	3.52	30.6
3	50:50	60.49	6.41	2.12	19.9
4	70:30	60.81	6.29	1.05	10.5
5	90:10	60.64	6.62	0.35	3.68

(shown in Figure 2), the signals of characteristic groups of the two fragments in the copolymers are overlapped. So it is difficult to determine the exact composition of these copolymers.

The actual composition of the copolymers, which was calculated from the elementary analysis data, is summarized in Table 2. The composition of the copolymer depends on the feed ratio of the monomers. When 1VI in the feed ratio is varied from 10% to 90%, the 1VI content in the copolymer is changed from 3.68% to 67.1%.

According to Table 2, the composition curve of the copolymers, F_1-f_1 (1: 1VI) curve, which can roughly describe the behavior of two monomers during the copolymerization, is shown in Figure 3. It is indicated in Figure 3 that this free radical copolymerization is a nonideal copolymerization, with $r_1 < 1$, $r_2 > 1$, and $r_1 r_2 < 1$.

Copolymerization reaction of 1VI with DIPVBP was carried out under low conversion ratio (<10%) to determine the reactivity ratios (r_1 and r_2) in the steady-state by using the well-known terminal model of the Kelen−Tudos[22] equation, which is the further development for the Finemann−Ross method. K−T, as shown in eq 1

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

where $\eta = G/(\alpha + H)$, $\xi = H/(\alpha + H)$, $\alpha = (H_{min} \times H_{max})^{1/2}$, $G = R(\rho - 1)/\rho$, $H = R^2/\rho$, $R = [M_1]/[M_2]$, and $\rho = d[M_1]/d[M_2]$. The reactivity ratios of the monomers (r_1 and r_2) were obtained using experimental data presented in Table 3 from the K−T plot (Figure 4) of ξ vs η.

The Kelen−Tudos plot gives the reactivity ratios of 1VI and DIPVBP, $r_1 = 0.10$ and $r_2 = 3.10$, respectively. The reactivity ratios also indicate that the imidazole moiety is surrounded by the phosphonate groups in the early stage of the copolymerization. As shown in Figure 5, there is no significant difference among the curves of samples 1, 3, and 5, which suggests that the feed ratio has little impact on the reaction rate. As general free radical polymerization, high initiator concentration leads to high reaction rate but low molecular weight (Table 4). Because of the higher molecular weight, there is significant automatic acceleration phenomenon in sample 7.

Thermal Analysis. TG analysis of the copolymers was performed under an air atmosphere. For the copolymer (sample 3) and PDIPVBP, a little weight loss of the samples appeared around 100 °C (Figure 6) can be attributed to the evaporation of physically bonded water. The sharp weight loss for the copolymer and PDIPVBP at 250 °C is mainly due to the degradation of the diisopropyl bond and ester of the vinylbenzyl phosphonate (VBP) moiety in the copolymer and PDIPVBP. The thermal degradation of VBP moiety at 240−250 °C is due to the loss of the ester group leading to the highly cross-linked network, resulting in the stability that the matrix exhibits between 270 and 400 °C.[25] As shown in Figure 6, the degradation of the main chain of the copolymer starts at a little higher temperature (450 °C) than those of P1VI (395 °C) and PDIPVBP (415 °C). It can be assumed that the cross-linked network formed between imidazole ring and phosphonic acid moiety in the copolymer provides the main chain with a little higher thermal stability than that formed among phosphonic acid groups in PDIPVBP.

DSC measurements were carried out to determine the glass transition temperatures (T_gs) of the copolymers and the homopolymers (Table 4). The T_gs of the copolymers increase from 31.4 to 120 °C with increasing content of imidazole ring in the copolymers, which are all between the T_gs of PDIPVBP (28 °C) and P1VI (158 °C). The increase in T_g is due to the influence of the hydrogen bonds which form between imidazole ring and phosphonate group as well as between imidazole ring and imidazole ring. While for the diisopropyl group, it is difficult to form the hydrogen bond among phosphonate groups. Without the steric hindrance, it is easy to construct the hydrogen bonds among imidazole rings in P1VI, which has a higher T_g at 158 °C. The results above can also be indicated from the IR spectrum of the copolymer and homopolymers, as shown in Figure 1. From Table 4, it can be shown that the T_gs of the copolymers also depend on the molecular weight. Higher molecular weight leads to higher glass transition temperature.

Solubility of Poly(VBPA-*co*-1VI). Poly(vinylbenzylphosphonic acid-*co*-1-vinylimidazole) was prepared by hydrolysis of the phosphonate ester groups in poly(DIPVBP-*co*-1VI)s. After hydrolysis, as is shown in Table 5, the solubility of the copolymers was changed. All poly(VBPA-*co*-1VI)s are insoluble in ethanol, while poly(DIPVBP-*co*-1VI)s can be dissolved in ethanol before hydrolysis, except sample 5 which contains more VBPA units. Sample 1, which was obtained at higher ratios of 1VI, is completely dissolved in water. Samples 2, 3, and 4 are only soluble in the ethanol with hydrochloric acid (1 mol/L) but cannot be dissolved in pure water or ethanol. That may be due to the construction of the hydrogen bond between imidazole ring and phosphonate group, which increases the polarity of the copolymers.

Proton Conductivity of Poly(VBPA-*co*-1VI). With the relative humidity (RH) of 100%, the proton conductivity of the membrane was determined by impedance spectroscopy in the temperature range from 30 to 95 °C (Figure 7). With high relative humidity, the proton conductivity of these materials increases gradually with increasing temperature, but the increment is small. The proton conductivity of poly(VBPA-*co*-1VI) is always much higher than that of PVBPA and increases with increasing 1VI content in the copolymer. Compared with phosphonic acid, which is a proton donor in the system, imidazole is a basic group and can act as a proton acceptor, which is a good supplement for water, another proton acceptor in the system. Besides this, the basicity of imidazole is higher than that of water. Thus, the proton conductivity of the

Table 3. Data of Relative Parameter for the K−T Method

	feed composition		copolymer composition					
sample	$[M_1]$ (mol %)	R	d$[M_1]$ (mol %)	ρ	G	H	ξ	η
1	90	9	67.1	2.04	4.59	39.7	0.92	0.11
2	70	2.33	30.6	0.44	−2.96	12.4	0.78	−0.19
3	50	1	19.9	0.25	−3.03	4.03	0.53	−0.40
4	30	0.43	10.5	0.12	−3.21	1.56	0.30	−0.62
5	10	0.11	3.68	0.04	−2.80	0.32	0.08	−0.72
$\alpha = (H_{min} \times H_{max})^{1/2} = 3.5803$								

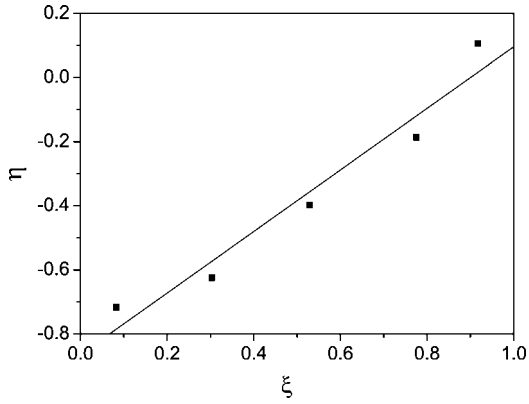

Figure 4. Kelen−Tudos plot for samples 1−5.

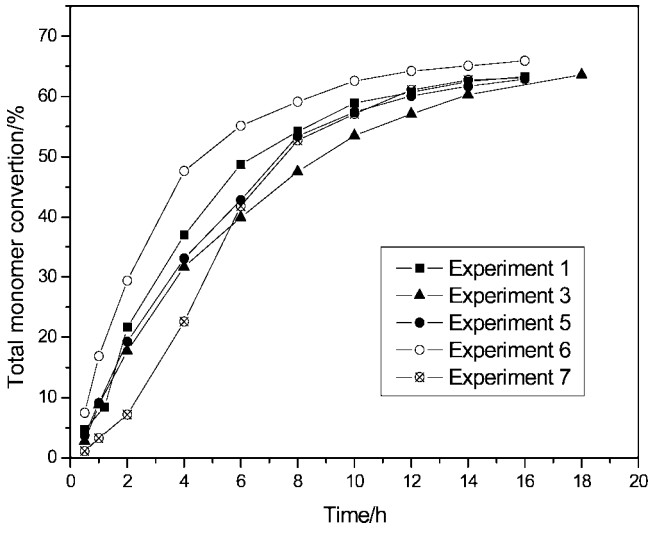

Figure 5. Total monomer conversion vs time of free radical copolymerization of DIPVBP and 1VI, carried out with the conditions shown in Table 1.

Table 4. Characteristics of the Copolymers and Homopolymers Synthesized

sample	P1VI[a]	1	2	3	5	6	7	PDIPVBP[a]
M_w					10260	3875	17362	
polydispersity					1.57	1.63	1.31	
T_g (°C)	158	120	65.4	36.6	31.4		36.4	28

[a] The homopolymers were synthesized at the same conditions as samples 1−5.

copolymer is improved significantly after the introduction of imidazole group in the copolymer.

It is also shown in Figure 7 that there is a drop for the proton conductivity of PVBPA at 80 °C, which is not observed in the curves of poly(VBPA-*co*-1VI). The decrease of the proton conductivity is due to the evaporation of the water inside PVBPA membrane. While for poly(VBPA-*co*-1VI), the imidazole can still act as the proton acceptor, even most of the water inside the membrane is evaporated. As shown in Figure 7, the

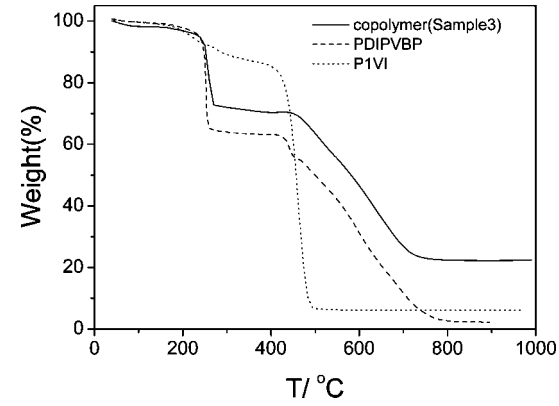

Figure 6. Thermal gravimetric analysis (TGA) of copolymer (sample 3), PDIPVBP, and P1VI.

Table 5. Solubility of Copolymers before and after Hydrolysis in Some Solvents[a]

	before hydrolysis					after hydrolysis				
	1	2	3	4	5	1	2	3	4	5
chloroform	+	+	+	+	+	−	−	−	−	−
ethanol	+	+	+	+	+	−	−	−	−	−
methanol	+	+	+	+	+	−	−	−	−	+
ethanol/HCl_{aq} solution (1 mol/L) (1/1, v/v)	−	−	−	−	−	+	+	+	+	+
water	−	−	−	−	−	+	−	−	−	−

[a] +: soluble (0.01 g of sample can be dissolved completely in 10 mL of solvent); −: insoluble.

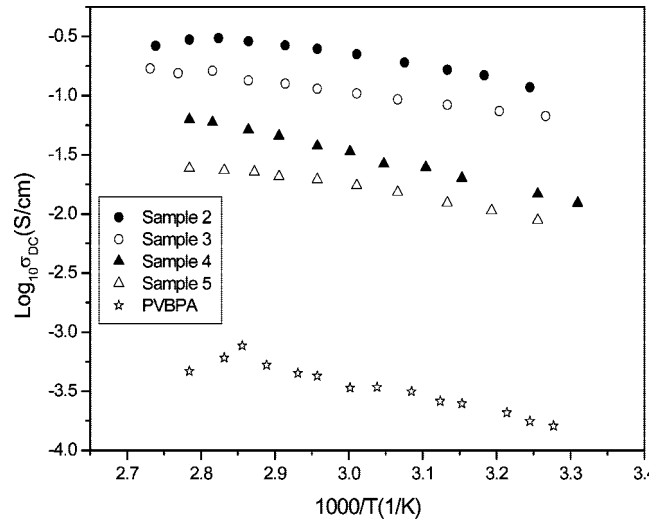

Figure 7. Temperature dependence of the proton conductivity of poly(VBPA-*co*-1VI) and PVBPA, relative humidity 100%.

proton conductivity of copolymers are high enough (10^{-1} S cm^{-1}at 30 °C) to be used as PEMs in the practical application.

Conclusion

A series of copolymers of vinylbenzylphosphonic acid and 1-vinylimidazole with various compositions were synthesized

via free radical copolymerization of diisopropyl-*p*-vinylbenzyl phosphonate and 1-vinylimidazole first and hydrolysis thereafter. The reactivity ratio of 1VI (r_1) and DIPVBP (r_2) were 0.10 and 3.10, respectively, which are calculated by the Kelen−Tudos method at low conversion (<10%). The copolymers are thermally stable up to 250 °C. The proton conductivity of poly(VBPA-*co*-1VI) is always much higher than that of PVBPA and increases with increasing 1VI content in the copolymer. With higher content of 1VI, the copolymer has a higher conductivity of 10^{-1} S cm^{-1}at 30 °C. Thus, the novel proton-conducting copolymers were obtained by immobilizing proton donor and acceptor in the same backbone.

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