Proton-Conducting Polymers via Atom Transfer Radical Polymerization of Diisopropyl-*p*-Vinylbenzyl Phosphonate and 4-Vinylpyridine

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ABSTRACT: Copolymerization of diisopropyl-*p*-vinylbenzyl phosphonate (DIPVBP) and 4-vinylpyridine (4VP) by atom transfer radical polymerization (ATRP) was studied in the presence of different catalyst systems using DMF as solvent. When a $Cu^{I}Br$ complex was used as catalyst and the reaction was carried at 90 °C in DMF, dramatically fast radical termination was observed and the chain propagation was almost stopped at an early stage of ATRP. $Cu^{I}Cl$ with different ligands were used as ATRP catalyst systems to modify the reaction conditions. An improved ATRP catalyst system was $Cu^{I}Cl$/*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine (HMTETA). The ^{1}H NMR technique was successfully applied online to investigate the kinetic parameters of atom transfer radical copolymerization (ATRCP) of DIPVBP and 4VP. The reactivity ratio of DIPVBP (r_{DIPVBP}) and 4VP (r_{4VP}) was 0.69 and 1.17, respectively, which were calculated with the Extended Kelen−Tudos method at high conversions (15−40%). A proton-conducting statistical copolymer (poly(vinylbenzyl phosphonic acid-*stat*-4VP)) was then obtained by complete hydrolysis of the phosphonate groups.

Introduction

Controlled/living radical polymerizations, including atom transfer radical polymerization (ATRP), are receiving increasing attention because they are powerful tools for macromolecular design: the synthesis of homopolymers or copolymers with narrow molecular weight distribution,[1–3] the synthesis of end-functionalized polymers by selective termination of the chain ends with various reagents,[4,5] the synthesis of novel statistical copolymers by the controlled addition of comonomers (e.g., semibatch copolymerization),[6–8] and the synthesis of polymers with interesting properties simply by varying the topologies (i.e., star, comb, dendritic, hyperbranched).[9–13]

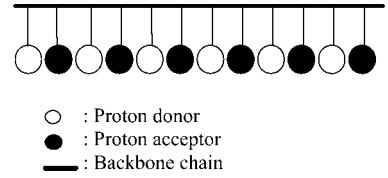
ATRP has been used successfully to prepare homopolymers and copolymers with different topologies by using multifunctional initiators, inimers, or macroinitiators.[10,13–15] Gradient copolymers, in which the instantaneous composition varies continuously along the chain, have been prepared by ATRP.[6] In a batch copolymerization using a controlled/living polymerization technique such as ATRP, a gradient is produced spontaneously due to the feed composition drift that occurs during the reaction.[16,17] In conventional free-radical polymerization this drift is manifested in a change in composition among the chains, whereas in living polymerization the change in composition occurs in each chain. In systems which obey the terminal model the composition drift can be explained by eq 1,

$$F_1 = \frac{r_1 f_1 + f_1 f_2}{r_1 f_1 + 2 f_1 f_2 + r_2 f_2} \quad (1)$$

where r_1 and r_2 are the reactivity ratios, f_1 and f_2 are the molar fractions of monomers 1 and 2, respectively, in the monomer feed, and F_1 is the molar fraction of units from monomer 1 in the copolymer.[18] Therefore, the design and simulation of a gradient copolymer with expected composition should be possible on the basis of an accurate estimation of the reactivity ratio of the monomers. Several pairs of comonomers have been polymerized by ATRP, and their reactivity ratios have been determined under certain conditions.[16,19–21] It has been reported that monomer pairs should have similar reactivity ratios in ATRP and conventional radical polymerization since in both methods propagation occurs though a free-radical mechanism.[21,22] However, some discrepancies in the value of reactivity ratios from ATRP and conventional radical polymerization have been observed.[23]

To the best of our knowledge, there is no report about either atom transfer radical homopolymerization or copolymerization of vinylbenzyl phosphonates in which the ester group can be completely hydrolyzed to obtain phosphonic acids. The phosphonic acid containing polymers are important for some applications. For example, phosphonic acid containing materials are considered to be most promising proton-conducting polyelectrolytes.[24–27] Heterocycle containing polymers such as poly(4-vinylpyridine) are also proton conductive in the presence of proton donors. For proton conduction, an ideal model of copolymers with both proton donor and acceptor units would be a strong alternating copolymer. Scheme 1 shows the ideal model of a proton conducting copolymers with both proton donors and proton acceptors. Reactivity ratios play a central

Scheme 1. Schematic Representation of the Ideal Model of Proton Conducting Copolymer with Both Proton Donors and Proton Acceptors



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role in the study and design of the copolymerization and are obtained by establishing the relationship between the compositions of the copolymer produced from various feed ratios. To achieve the microscopic design of the molecular chain, further investigation of a unique combination of the catalytic system, solvent, temperature for the ATRP of diisopropyl-*p*-vinylbenzyl phosphonate (DIPVBP) and 4-vinylpyridine (4VP), and the accurate estimation of the reactivity ratios of the monomer pairs are of great significance.

Among several procedures available to determine monomer reactivity ratios, the methods of Mayo−Lewis,[18] Finemann−Ross,[28] inverted Finemann−Ross,[29] Kelen−Tudos (K-T),[30] extended Kelen−Tudos,[31,32] Tidwell−Mortimer,[33] and Mao−Huglin[34] are extensively used. The extended K-T method is a linear least-squares (LLS) method that can be applied both at low conversions (<15%) and medium-high conversions (<40%).[35] In conventional free-radical polymerization, high polymers are formed at the beginning of the reaction and the composition of the polymer is established at low conversion, while in ATRP, a high polymer is not formed immediately. At the beginning of the reaction, one monomer may react preferentially affected by the initiator. Therefore, in ATRP, a medium-high conversion (20−50%) is appropriate for the determination of the reactivity ratios of the comonomers. [6]

In the present work, the ^{1}H NMR technique has been applied online to investigate the kinetic parameters of atom transfer radical copolymerization (ATRCP) of DIPVBP and 4VP. This technique is informative and effective when the vinylic proton signals from each monomer are nonoverlapping with each other.

Experimental Section

Materials. The initiator, ethyl-2-bromoisobutyrate (EBiB, 98%, Aldrich) was used as received, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 98%, Alfa Aesar) was freshly distilled prior to use. The monomer, 4VP (96%, Alfa Aesar) was distilled twice under reduced pressure over NaOH pellets and stored at −18 °C under Ar. DIPVBP was prepared according to the literature.[36] tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was prepared according to the literature.[37] Cu^{I}Br (99.999% Aldrich), Cu^{I}Cl (99.999% Aldrich), vinylbenzyl chloride (97%, Aldrich), diisopropyl phosphite (98%, Alfa Aesar), potassium *tert*-butoxide (98%, Acros Organics), bromotrimethylsilane ($BrSi(CH_3)_3$, 98%, Acros Organics), *N*,*N*,*N*′,*N*″,*N*‴,*N*‴- hexamethyltriethylenetetramine (HMTETA, Aldrich), and the other chemicals were used as received.

Synthesis of DIPVBP. The monomer diisopropyl-*p*-vinylbenzyl phosphonate was synthesized in a method adapted from the literature.[36] Isopropyl phosphite (14.19 g, 85.4 mmol) and vinylbenzyl chloride (10.72 g, 70.25mmol) were dissolved in dry THF to obtain solution A. Potassium *tert*-butoxide (8.16 g, 72.7mmol) was dissolved in 40 mL of dry THF and was then added dropwise to solution A during a period of 1 h cooled occasionally with an ice bath. The mixture was kept stirring for another 2 h at room temperature and then filtered, diluted with diethyl ether, and washed with deionized water three times. The raw product was then purified by flash column chromatography on silica. ^{1}H NMR: δ 7.28 (d, 2H, Ar−H), 7.21 (dd, 2H, Ar−H), 6.63 (dd, 1H, CH═C**H**$_2$), 5.69 (d, 1H, CH═C**H**$_2$), 5.20 (d, CH═C**H**$_2$), 4.57 (m, 2H, CH $(CH_3)_2$), 3.06 (d, 2H, CH_2−P), 1.21 (d, 6H, CH3), 1.16 (d, 6H, CH3). ^{13}C NMR: δ 23.69 (d, CH_3), 23.98 (d, CH_3), 33.60 (d, CH_2−P), 70.53 (d, CH−O), 113.41 (CH_2═CH), 126.10 (CH═CH_2), 130.0 (d, Ar−H), 131.6 (d, Ar−CH_2), 135.93 (Ar−CH), 136.42 (Ar−H).

Atom Transfer Radical Copolymerization. A mixture of 4VP, DIPVBP, EBiB (0.0195 g, 0.1mmol), PMDETA or HMTETA or Me_6TREN (0.1mmol), and dry DMF (0.73 g, 10mmol) was added to the flask and frozen in liquid nitrogen. Cu^{I}Cl (0.0099 g, 0.1mmol) (Cu^{I}Br (0.0144 g, 0.1mmol)) was then added and the mixture was degassed by three freeze–pump–thaw cycles under Ar. A small amount of the mixture was stringed into an Ar-degassed NMR tube and sealed. All the samples were freshly prepared and stored at −18 °C shortly before the online ^{1}H NMR measurements and reactions were started at elevated temperatures (90 °C, +0.1 °C). In this work, the total monomer/initiator/catalyst/ligand/solvent molar ratio was fixed as 200:1:1:1:100. PMDETA, HMTETA, and Me_6TREN were used as ligand for ATRP. Reaction conditions for statistical ATRCP of DIPVBP and 4VP at 90 °C are listed in Table 1. All kinetic measurements were carried out on a Bruker Avance 300 NMR spectrometer (Bruker Instruments, Germany).

Table 1. Reaction Conditions for Statistical Copolymerizations of DIPVBP and 4VP at 90 °C

experiment	monomer feed molar ratio (DIPVBP/ 4VP)	$[M]_0$:$[I]_0$: $[CuCl]_0$:$[ligand]_0$
1	100:100	200:1:1[a]:1 (PMDETA)[b]
2	100:100	200:1:1[a]:1 (PMDETA)
3	100:100	200:1:1:1 (PMDETA)
4	100:100	200:1:1:1 (Me_6-TREN))
5	100:100	200:1:1:1 (HMTETA)
6	180:20	200:1:1:1 (HMTETA)
7	140:60	200:1:1:1 (HMTETA)
8	60:140	200:1:1:1 (HMTETA)
9	20:180	200:1:1:1 (HMTETA)

[a] CuBr. [b] At 60 °C.

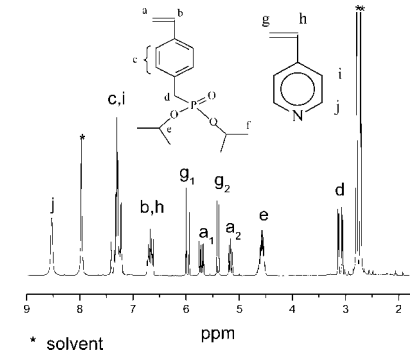

Figure 1. ^{1}H NMR Spectrum of the Reaction Mixture of ATRCP of DIPVBP and 4VP at $t = 0$.

Characterization of DIPVBP-*stat*-4VP Copolymers. Gel permeation chromatography (GPC) measurements were conducted to determine the molecular weights of copolymers on the basis of a polystyrene standard. Copolymers prepared by experiments 5–7 were eluted with DMF at 60 °C using a Waters 515 liquid chromatograph pump (1.0 mL/min) and three Polymer Standards Service columns (GRAM 10000, 1000, 100). Copolymers prepared by experiments 8 and 9 were eluted with a mixture of 80% aqueous solution (0.5 M Na_2SO_4, 0.5 M CH_3COOH) and 20% CH_3CN at 23 °C using a Waters 515 liquid chromatograph pump (1.0 mL/min) and three Polymer Standards Service columns (TSK Gel G6000, G5000, G3000).

Monomer Conversion and Reactivity Ratio Determination. Figure 1 shows the ^{1}H NMR spectrum of a reaction mixture at the beginning of the measurement. The vinylic proton signals from each monomer were well separated, and the variety of each monomer concentrations can be continuously collected by comparing the integral of the vinylic proton signals from the monomers to a standard which remained constant during the reaction. In this work, we set the peak (δ 4.57) which refers to the single proton of the isopropyl group as a standard. The conversion at each time (χ_t) for monomers could be computed according to the following equation (eq 2),

$$\chi_t = \frac{A_0 - A_t}{A_0} \tag{2}$$

where A_0 is the primary normalized integral of the characteristic monomer peak ($t = 0$) and A_t is the normalized integral of the characteristic monomer peak at time t. The cumulative composition of monomer 1 (F_t^1) and monomer 2 (F_t^2) at time t could be found using the following equations (eqs 3 and 4),

$$F_t^1 = \frac{A_0^1 - A_t^1}{[A_0^1 - A_t^1] + [A_0^2 - A_t^2]} \quad (3)$$

$$F_t^2 = \frac{A_0^2 - A_t^2}{[A_0^1 - A_t^1] + [A_o^2 - A_t^2]} \quad (4)$$

The extended K-T method was applied to estimate the reactivity ratios of the comonomers.

Preparation of Poly(vinylbenzyl phosphonic acid-*stat*-4VP). Two methods were applied to hydrolyze the phosphonate ester groups in DIPVBP-*stat*-4VP copolymers. (1) Copolymers prepared by experiments 5–7 were hydrolyzed using the method adapted from the literature.[38] Into a round-bottom flask, DIPVBP-*stat*-4VP copolymers were dissolved in CH_2Cl_2, excess of $BrSi(CH_3)_3$ (~5 times of the phosphonate group) was added dropwise into the solution at 0 °C. The mixtures were kept stirring under dry nitrogen for another 12 h at room temperature. Then, the solvent and volatile residues were evaporated under reduced pressure. Excess methanol was introduced, and the mixture was stirred at room temperature for 12 h. Poly(vinylbenzyl phosphonic acid-*stat*-4VP) was then obtained by precipitation in diethyl ether and drying under vacuum. (2) Copolymers prepared by experiments 8–9 were dissolved in water and reacted with excess HBr at 100 °C for 48 h, and the corresponding vinylbenzyl phosphonic acid-*stat*-4-vinyl pyridine copolymers were obtained after purification.

Proton Conductivity Measurement. The proton conductivity was measured by dielectric spectroscopy in a two-electrode geometry using an SI 1260 impedance/gain-phase analyzer. The humidity of air during data acquisition was set by mixing dry nitrogen with humidity saturated nitrogen. The relative humidity (RH) was measured using a Sensiron SHT15 sensor.

In order to determine the amount of water sorption, the samples were stored under an atmosphere of fixed humidity and temperature for several days. The humidity was set by saturated salt solutions according to literature data. [39] The uptake of water was measured on a Mettler MX5 microbalance until constant weight, *W*, was obtained; the water sorption was calculated from eq 5.

$$\text{wateruptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (5)$$

The samples for conductivity measurements were pressed into tablets and contacted by e-tek and stainless steel electrodes.

Results and Discussion

ATRCP of DIPVBP and 4VP. ATRP of DIPVBP was previously performed in our laboratory. Successful ATRP of DIPVBP could be achieved by using a copper(I) complex as catalyst and PMDETA, HMTETA, or Me6-TREN as ligand at 90 °C in the bulk. However, 4VP is a coordinating monomer and the nucleophilic part will effect the reaction in different ways.[40,41] DMF was used in order to obtain homogeneous reaction mixtures due to the bad solubility of 4VP and its polymer in less-polar solvents. ATRCP of DIPVBP and 4VP using CuBr as catalyst has a faster reaction rate than that using CuCl due to the higher activity of the bromide complex (see Figure 2). However, significantly fast radical elimination was observed when the reaction was carried out at 90 °C in DMF using CuBr as catalyst. Several factors presumably contributed to the chain termination. Generally, nonpolar solvents are preferred for ATRP because certain polymer end groups, such as polystyryl halides, can undergo solvolysis or elimination of HX at elevated temperature.[13] A slower chain termination was observed when the same reaction was performed at a lower temperature (60 °C); however, the reaction rate was very slow. Another possible reason is that interactions between the halide-ended chains and pyridine groups also make contribution to the chain termination. For this study, the effect of different copper(I) halide complexes and 4VP concentrations were investigated.

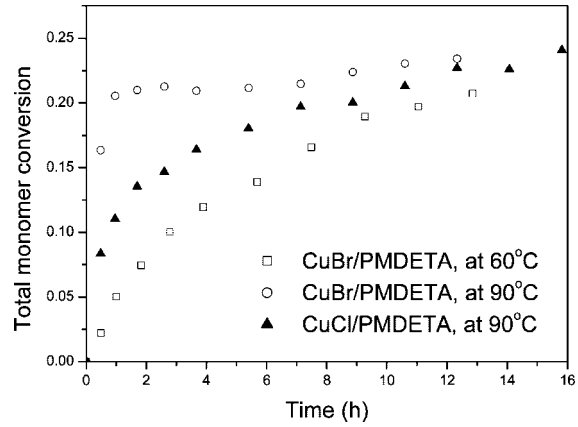

Figure 2. Total monomer conversions vs time of ATRP of DIPVBP-*co*- 4VP carried out with the conditions shown in Table 1 (experiments 1–3).

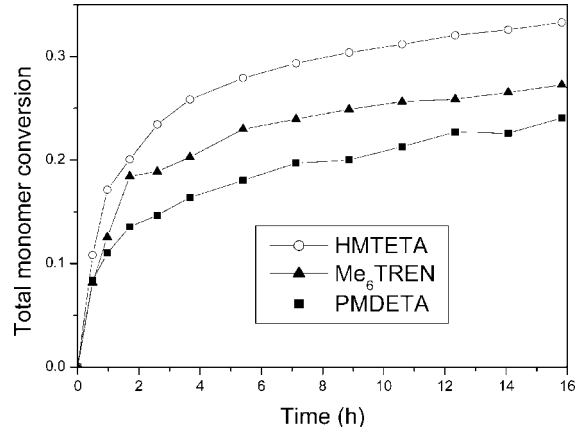

Figure 3. First-order plots of ATRP of DIPVBP-*co*- 4VP with various monomer feed ratios. Reaction conditions are given in Table 1 (experiments 5–8).

As can be derived from Figure 2, a slower chain termination could be observed when catalyst CuBr was replaced by CuCl. The reaction of bromide-ended poly(4VP) chains with pyridine units was also observed and investigated by Matyjaszewski and co-workers[41] who claimed that this reaction could be avoided when CuCl was used. Various deviations from the initial reaction rates in the first order plots can be seen in Figure 3 with different 4VP concentrations. The curvatures appearing in the first-order plots indicate the occurrence of chain termination. As we can derive from Figure 3, chain termination rates increase with the increasing concentration of 4VP which shows that pyridine units do affect the chain termination.

Due to the specialties of ATRCP of DIPVBP and 4VP, appropriate ligands should be selected to improve the polymerization. Since the kinetic chain length of a radical polymerization is proportional to the ratios of the monomer-to-radical concentrations and of propagation-to-termination rate constants, in order to increase the monomer conversion, an elevated reaction rate was expected when using an appropriate ligand. CuCl/PMDETA, CuCl/HMTETA, CuCl/Me_6TREN was used, respectively, as the catalyst system in ATRP of DIPVBP-*co*-4VP carried out in DMF at 90 °C. By comparing these three ligands, higher monomer conversions and reaction rates were obtained by using CuCl/HMTETA as the catalyst system (see Figure 4).

Monomer Reactivity Ratios Determination. Relative concentrations of each monomer during the copolymerization process were obtained simultaneously by comparing the normal-

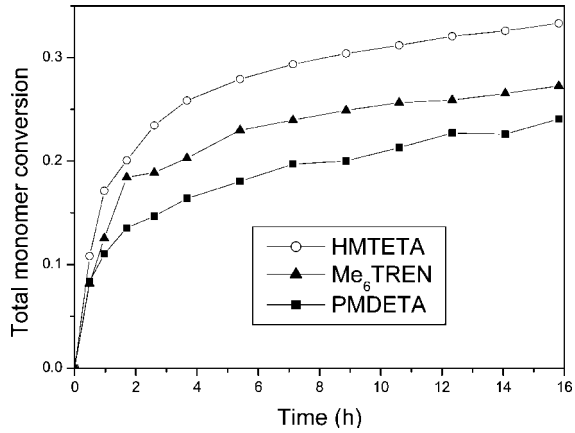

Figure 4. Total monomer conversions vs time of ATRP of DIPVBP-*co*- 4VP using different ligands. Reaction conditions are given in Table 1 (experiments 3–5).

Table 2. Results of GPC of DIPVBP-*stat*-4VP Copolymers

experiments	monomer feed ratios DIPVBP/4VP (molar ratio)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
5	50:50	5.0	11.9	2.4
6	90:10	9.2	24.1	2.6
7	70:30	7.0	11.8	1.7
8	30:70	7.5	16.8	2.2
9	10:90	11.1	17.9	1.6

Table 3. Copolymer Compositions from Kinetic Data and from ^{1}H NMR Spectra

experiment	monomer feed ratios DIPVBP/4VP (molar ratio)	*F* (DIPVBP/4VP) (molar ratio)	
		kinetic data	^{1}H NMR
5	50:50	41:59	43:57
6	90:10	85:15	83:17
7	70:30	62:38	61:39
8	30:70	27:73	25:75
9	10:90	11:89	8:92

ized integral of the vinylic proton signals from the monomers. ATRCP of DIPVBP and 4VP with various feed ratios were carried out using CuCl/HMTETA catalyst system in DMF at 90 °C. All reactions were initiated by EBiB. The calculated parameters needed for the determination of reactivity ratios are shown in Table 3. The obtained reactivity ratio is 0.69 for DIPVBP and 1.17 for 4VP.

Characterization of DIPVBP-*stat*-4VP Copolymers. The copolymers for GPC measurements were isolated and purified after 22 h of polymerization. The result (see Table 2) shows that the molecular weight distributions of the copolymers are broad ($M_w/M_n > 1.5$). However, in this work, no preformed deactivator ($CuCl_2$) was used to control the polymerization. The deactivator decreases the reaction rate, which may lower the monomer conversions and molecular weights in the presence of significant chain termination or transfer reactions.

Copolymer Compositions. The cumulative compositions of each monomer at a certain time *t* were calculated from monomer conversions during the copolymerization using eqs 3 and 4. The results show that the compositions of the copolymers mostly depend on the monomer feed ratios due to the close value of reactivity ratios of DIPVBP (0.69) and 4VP (1.17). Therefore, various copolymer compositions can be achieved by simply changing the feed ratios of DIPVBP and 4VP.

The compositions of isolated copolymers were also determined by ^{1}H NMR. Figure 5 shows the ^{1}H NMR spectra of DIPVBP-*stat*-4VP copolymers from which the copolymer compositions can be calculated. The copolymer compositions

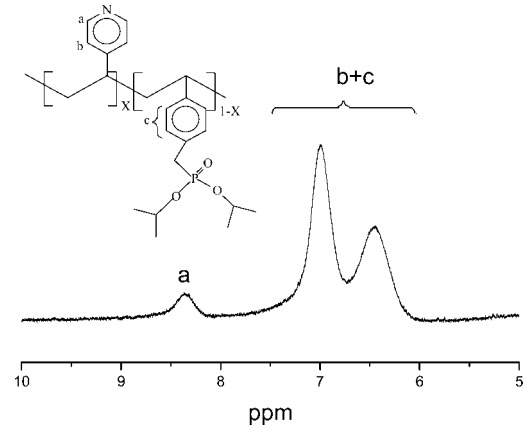

Figure 5. Peaks used for the polymer composition calculation in ^{1}H NMR spectra of typical DIPVBP-*stat*-4VP copolymers.

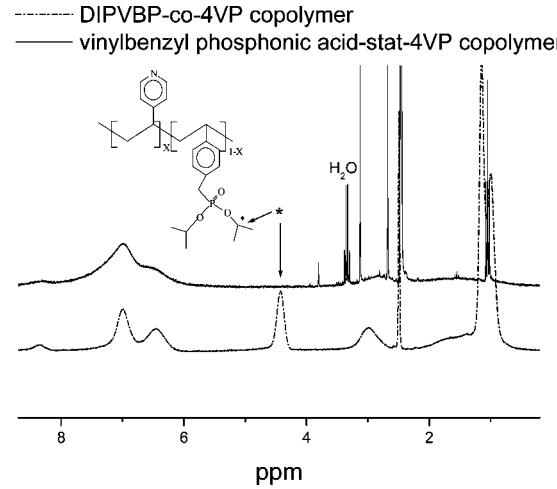

Figure 6. ^{1}H NMR spectra of a typical DIPVBP-*stat*-4VP copolymer and its corresponding vinylbenzyl phosphonic acid-*stat*-4VP copolymer.

from kinetic data are similar to that from ^{1}H NMR spectra (see Table 3).

Preparation and Characterization of Poly(vinylbenzyl phosphonic acid-*stat*-4VP). Poly(vinylbenzyl phosphonic acid-*stat*-4VP) was prepared by complete hydrolysis of the phosphonate ester groups in DIPVBP-*stat*-4VP copolymers. Figure 6 shows the ^{1}H NMR spectrum of a typical DIPVBP-*stat*-4VP copolymer and its corresponding vinylbenzyl phosphonic acid-stat-4VP copolymer. The labeled peak (δ 4.57) is the signal from the single proton of the isopropyl group. In the spectrum of vinylbenzyl phosphonic acid-*stat*-4VP copolymer this peak cannot be detected, which indicates a complete hydrolysis of DIPVBP-*stat*-4VP copolymer.

Poly(vinylbenzyl phosphonic acid) is hydrophilic but water-insoluble, while poly (4-vinylpyridine) is water-soluble. The water solubility of the vinylbenzyl phosphonic acid-*stat*-4VP copolymers varies with the copolymer composition. In the present work, water -soluble copolymers were only obtained with relatively high content of 4VP (e.g., 75% or 92%, molar ratio). For the application as proton exchange membranes (PEM), water up-taking materials are preferred because of their high conductivity in the presence of high humidity. However, good dimensional stability of PEM exposed to high humidity is also required. Therefore, hydrophilic but water-insoluble materials would be promising. Copolymers of vinylbenzyl phosphonic acid-*stat*-4VP with various water up-taking properties can be obtained by changing the polymer composition.

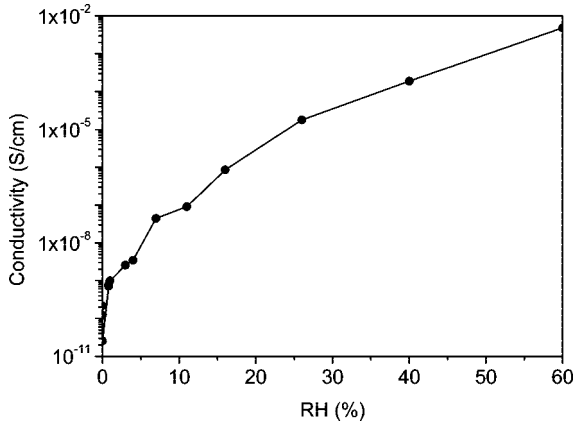

Figure 7. Proton conductivities of poly(vinylbenzyl phosphonic acid-*stat*-4VP) (90% 4VP in molar ratio) at 25 °C versus relative humidity.

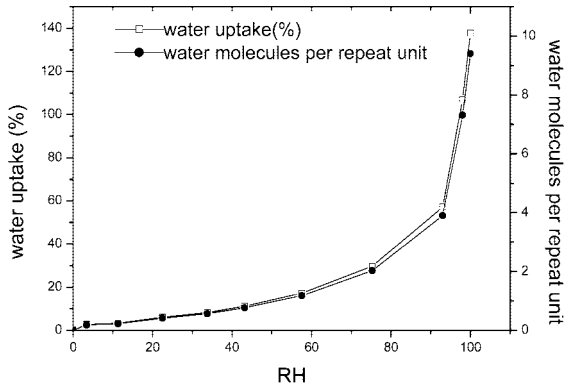

Figure 8. Water uptake at different relative humidity (RH) at 25 °C of poly(vinylbenzyl phosphonic acid-*stat*-4VP) (90% 4VP in molar ratio).

Proton Conductivity. Figure 7 shows the relative humidity effects on proton conductivities of poly(vinylbenzyl phosphonic acid-*stat*-4VP) (90% 4VP in molar ratio). The proton conductivity rises by several orders of magnitude with increasing water content. At a relative humidity of 60%, the proton conductivity reaches up to 10^{-2} S/cm at 25 °C. The corresponding water content at each RH is shown in Figure 8.

Conclusions

ATRCP of DIPVBP and 4VP was carried out successfully in DMF at 90 °C using $Cu^{I}Cl$/ HMTETA catalyst system. Typically, copper bromide-based ATRP catalysts provide better polymerization control than copper chloride-based systems. However, for different monomers, a unique combination of catalyst, ligand, solvent, temperature, and reaction time should be applied for achieving successful ATRPs. In this work, the reactivity ratio of DIPVBP (r_{DIPVBP}) and 4VP (r_{4VP}) were 0.69 and 1.17, respectively, calculated by the extended Kelen−Tudos method at high conversions. A series of vinylbenzyl phosphonic acid-*stat*-4VP copolymers with various copolymer compositions were obtained.

At a low hydration level (1.1 water/repeat unit), the copolymer with 90% 4VP in molar ratio had a high conductivity of 10^{-2} S/cm at 25 °C. A comprehensive study of proton conductivities of these vinylbenzyl phosphonic acid-*stat*-4VP copolymers and a further investigation of their other properties as PEM will be reported later.

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