Cationic Polymerization of Isobutyl Vinyl Ether Coinitiated with Heteropolyacid or its Salts in Aqueous Medium

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ABSTRACT: The suspension cationic polymerization of isobutyl vinyl ether (IBVE) in aqueous medium could be achieved by using $H_3PW_{12}O_{40}$, $AIPW_{12}O_{40}$, $FePW_{12}O_{40}$, $K_3PW_{12}O_{40}$, or $Na_3PW_{12}O_{40}$ as efficient water-tolerant coinitiators in the presence of HCI. The addition reaction of IBVE with H_2O occurred to form IBVE– H_2O adduct and then subsequent decomposition immediately took place or turned to acetaldehyde diisobutyl acetal (A) in the presence of AIPW₁₂O₄₀, and (A) decomposed rapidly to form 2-isobutanol (B) and acetaldehyde (C). Cationic polymerization of IBVE in aqueous medium was promoted greatly with increasing HCl concentration and proceeded extremely rapidly to get high polymer yield even at low concentration of AIPW₁₂O₄₀ of 0.3 mM. A sufficient amount of HCl was needed to decrease the hydrolysis of initiator IBVE–HCl and to accelerate the polymerization in aqueous

INTRODUCTION The controlled/living cationic polymerizations of vinyl monomers, such as isobutylene, styrene (St), or isobutyl vinyl ether (IBVE) have been achieved by using initiator/coinitiator initiating system in organic solvent under strictly anhydrous conditions, in which the coinitiator is Lewis acid, such as AlCl₃, TiCl₄, BF₃, SnCl₄, AlEtCl₂, AlMeCl₂, or ZnI₂.¹ All these Lewis acids are moisture-sensitive and decomposed in the presence of water.² Conversely, in general, the presence of water above certain concentration will terminate the cationic polymerization.² Boron trifluoride etherate (BF3 ·OEt2) was used for cationic polymerization of styrene and its derivatives only in the presence of a small amount of water.^{3,4} However, water is an economically environmental-friendly green solvent in chemical reactions. Thus, the cationic polymerizations in aqueous medium really become a big challenge in this area.^{2,5}

Several research groups have focused on the cationic polymerization of vinyl monomer in aqueous medium recently.⁵⁻¹¹ Lanthanide triflates was introduced as a water-tolerant Lewis acid in cationic polymerization of certain monomers including IBVE and *p*-methoxystyrene (*p*MOS) in the presence of water.⁵⁻⁹ Sawamoto and his coworkers⁶ reported that cationic medium simultaneously. The yield and molecular weight of poly(IBVE) increased with increasing concentrations of HCl and AIPW₁₂O₄₀ or with decreasing temperature. The isotactic-rich poly(IBVE)s with *m* diad of around 60%, having M_n of 1200–4500 g mol⁻¹ and monomodal molecular weight distribution could be obtained via cationic polymerization of IBVE in aqueous medium. This is the first example of cationic polymerization of IBVE in aqueous medium coinitiated by heteropolyacid and its salts. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 546–556

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polymerizations of pMOS or IBVE could be induced by using rare earth metal triflate $[Ln(OTf)_3; Ln = Yb, Sc, Dy, Sm, Gd,$ and Nd; $OTf = OSO_2CF_3$] in conjunction with hydrogen chloride-vinyl monomer adduct in aqueous medium. The cationic polymerization of *p*MOS in aqueous medium was quite slow to reach 98% of monomer conversion after polymerization for 200 h, and poly(*p*MOS)_s with $M_{\rm n}$ of 2000–4000 g mol⁻¹ were obtained.⁶ The cationic polymerizations of pMOS could also be carried out with Lewis acid-surfactant combined catalysts, such as trisdodecyl sulfate ytterbium starting from Lewis acid YbCl₃ or Yb(OTf)₃.^{5,7} Photoinitiated cationic polymerization of IBVE in aqueous medium was conducted by using diphenyliodonium iodide in the presence of Yb(OTf)₃, resulting in low molecular weight ($M_n \sim 2000 \text{ g mol}^{-1}$).⁸ Transition metal (Sn, Zn, and Cu) triflates and their tetrafluoroborates were also used as water-tolerant Lewis acids for emulsion cationic polymerization of pMOS in heterogeneous aqueous medium, while it took long time (\sim 100 h) to get high monomer conversion of 90%.⁶ The miniemulsion cationic polymerization of pMOS could be carried out by dodecylbenzenesulfonic acid and surfactant (INISURF), leading to low $M_{\rm n}$ (~1000 g mol⁻¹), and $M_{\rm n}$ increased slowly with monomer conversion due to critical degree of polymerization (DP) effect when monomer

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conversion \geq 20%. Stable inverse emulsion cationic polymerization of *p*MOS was conducted in water by using DBSA/ Yb(OTf)₃ system to produce low molecular weight polymers ($M_n = 1000-3000 \text{ g mol}^{-1}$).⁹

Tri(pentafluorophenyl)borane, $B(C_6F_5)_3$ was also reported as an effective water-tolerant Lewis acid for cationic polymerizations of *p*MOS, styrene, cyclopentadiene, or isoprene in aqueous medium to produce the corresponding polymers with low molecular weight ($M_n < 4000 \text{ g mol}^{-1}$) and having hydroxyl terminal groups.¹⁰ The cationic polymerization of isobutylene in aqueous suspension could be induced by using chelating diboranes (C_6F_4 -1,2-[$B(C_6F_5)_2$]) as coinitiatortor.¹¹

Heteropolyacid has been widely used in organic synthesis and in polymerization. Dodecatungstophosphate acid $(H_3PW_{12}O_{40})$ was provided as an efficient catalyst in bulk cationic polymerization of tetrahydrofuran (THF) using ethylene oxide as promoter to produce polyTHF with M_n in the range of 1000–3000 g mol^{-1.12} The bulk or solution polymerizations of IBVE, styrene, and IB in dry organic solvents were carried out with H₃PW₁₂O₄₀, resulting in formation of low molecular weight polymers ($M_{\rm n}$ < 3000 g mol⁻¹).¹²⁻¹⁸ $H_3PW_{12}O_{40}$, 12-molybdophosporic acid ($H_3MoW_{12}O_{40}$) and their homologous salts (NH₄)₃PW₁₂O₄₀, (NH₄)₃MoW₁₂O₄₀ were used to initiate cationic polymerization of styrene in CH_2Cl_2 , and $H_3PW_{12}O_{40}$ has the highest catalytic activity due to the acidity strength order of $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} >$ $(NH_4)_3 PW_{12}O_{40} > (NH_4)_3 PMo_{12}O_{40}$.^{15,16} The heterogeneous living cationic polymerization of IBVE could be achieved by using $H_3PW_{12}O_{40}$ in the presence of Me_2S at $-30\ ^\circ C.^{17}$ Very recently, living cationic polymerization of IBVE could be achieved by using HCl in the presence of ether as the HCl·Et₂O acts as protonogen and plays both as an activator and initiator.¹⁷ (NH₄)_{2.5}H_{0.5}PW₁₂O₄₀ was used to coinitiate the cationic polymerization of IB in an inert hydrocarbon solvent to produce highly reactive polyisobutylenes.¹⁸ Aluminum dodecatungstophosphate ($AlPW_{12}O_{40}$) is a highly water-tolerant Lewis acid and an efficient catalyst for organic synthesis, such as protection of thiols and chemoselective synthesis of geminal diacetates (acylals) in CH₃CN or CH_2Cl_2 solution but never for cationic polymerization of vinyl monomer in aqueous medium.¹⁹ Therefore, we extended our study to the cationic polymerization of IBVE with $AlPW_{12}O_{40}$ or other salts, such as $FePW_{12}O_{40}$, $K_3PW_{12}O_{40}$, and $Na_3PW_{12}O_{40}$ in the presence of large amount of water in this current paper.

RESULTS AND DISCUSSION

Cationic Polymerization of IBVE with IBVE-HCl/ AlPW₁₂O₄₀ Initiating System in CH₂Cl₂

The control experiments of heterogeneous cationic polymerization of IBVE were performed using $AlPW_{12}O_{40}$ in conjunction with IBVE–HCl in CH_2Cl_2 at 0 °C for comparison. Lewis acid $AlPW_{12}O_{40}$ activated the C—Cl bond in IBVE–HCl to induce cationic polymerizations. The representative gel permeation chromatography (GPC) traces of resulting poly(IBVE)s and the data of polymer yield, M_{n} , and molecu-



FIGURE 1 GPC traces of poly(IBVE) obtained from cationic polymerization of IBVE in CH_2CI_2 at different times at 0 °C. [IBVE] = 1 M, AIPW₁₂O₄₀ = 30 mg, [IBVE-HCI] = 25 mM.

lar weight distribution (MWD) (M_w/M_n) are given in Figure 1. It can be seen from Figure 1 that cationic polymerization of IBVE in CH₂Cl₂ proceeded rapidly to get 30% of polymer yield after 2 min and 100% of polymer yield after 20 min, and poly(IBVE)s with M_n of 4100–4700 g mol⁻¹ and monomodal MWD ($M_w/M_n = 2.4$ –2.7) could be obtained. The M_n kept almost unchanged and number of polymer chains (N) increased gradually from 1.46 × 10⁻⁵ mol to 4.76 × 10⁻⁵ mol with prolonging polymerization time from 2 to 20 min. These experimental results indicate that slow initiation and rapid propagation took place in the heterogeneous cationic polymerization of IBVE coinitiated by AlPW₁₂O₄₀ in CH₂Cl₂.

The chemical structure of terminal groups in poly(IBVE) was examined by NMR spectroscopy, and the representative ¹H and ¹³C NMR spectra are shown in Figure 2(a,b) respectively. It can be clearly observed from Figure 2(a) that the characteristic signal at $\delta = 1.15$ ppm is assigned to $-CH_3$ group (peak 1) at head group of poly(IBVE) chain. Conversely, the characteristic resonances at $\delta = 4.56$ ppm and $\delta = 9.81$ ppm are assigned to -CH-O- (peak 7), and -CH=O (peak 10) terminal groups, respectively. The content of -CH-Oterminal group was determined to be 74% as polymerization was quenched with CH₃OH or *i*-BuOH.^{20,21} There was no signal (δ = 6.1 ppm) belonging to the structure of -CH=CH-OiBu due to β -elimination. The ¹³C NMR analysis in Figure 2(b) was applied to examine stereoregularity of the resulting poly(IBVE) chains, and the meso diad was determined to be 67%, which is a similar value to those of poly(IBVE) obtained with various metal halides in organic solvents.1

Moreover, the cationic polymerization of IBVE in CH_2Cl_2 could also be induced with $H_2O/AIPW_{12}O_{40}$ initiating system





FIGURE 2 ^1H and ^{13}C NMR spectra of poly(IBVE) (P_3) in CH_2Cl_2 at 0 °C.

in the absence of IBVE–HCl. Compared to the cationic polymerization of IBVE with IBVE–HCl/AlPW₁₂O₄₀ initiating system in CH₂Cl₂, cationic polymerization of IBVE with H₂O/AlPW₁₂O₄₀ initiating system in CH₂Cl₂ proceeded relatively slowly and produce 33% of polymer after 20 min and 96% of polymer after 60 min, respectively.

Cationic Polymerization of IBVE coinitiated by $AIPW_{12}O_{40}$ in Aqueous Medium

Suspension cationic polymerization of neat IBVE with $AlPW_{12}O_{40}$ coinitiator was conducted in aqueous medium in the absence of IBVE-HCl at 0 °C. Unexpectedly, no polymer

could be obtained but oil-like organic phase was formed in the reaction system. Therefore, it is necessary to get deep investigation on the reason for no polymerization of IBVE coinitiated by $AIPW_{12}O_{40}$ in water. The oil-like organic phase was taken out at different reaction times for ¹H NMR characterization, and the corresponding ¹H NMR spectra are given in Figure 3. The characteristic resonances at $\delta = 0.96$ ppm (peak a), $\delta = 1.98$ ppm (peak b), and at $\delta = 3.97$ ppm (peak c) are assigned to methyl, methane, and methylene groups of IBVE, respectively. Surprisingly, it can be observed that the characteristic resonances at $\delta = 6.52$ ppm (peak d) for --CH= and $\delta = 4.16$, 3.95 ppm (peak e) for =-CH₂ of IBVE



FIGURE 3 ¹H NMR spectra of reaction mixtures of IBVE with water in the presence of $AIPW_{12}O_{40}$ at 0 °C. IBVE = 1 mL (7.7 mmol), $[AIPW_{12}O_{40}] = 26$ mM in water. $H_2O = 1$ mL.



FIGURE 4 IBVE conversion (a) and **A**% (b) with reaction time in aqueous medium at different concentrations of AIPW₁₂O₄₀. IBVE = 7.7 mmol, $H_2O = 1$ mL, $T_p = 0$ °C.

reduced gradually with prolonging reaction time and finally disappeared. It means that IBVE had been converted to other compounds in the presence of $AlPW_{12}O_{40}$. The extremely unstable hemiacetal (IBVE-H₂O) formed by addition of double bond of IBVE with H_2O catalyzed by $AIPW_{12}O_{40}$ and then rapidly decomposed to 2-isobutanol (B) and acetaldehyde (C). The decomposition of unstable hemiacetal to acetaldehyde was also observed in termination under the similar conditions in ref. 20 The characteristic resonances at δ = 3.35 ppm (peak m) for $-CH_2$ in 2-isobutanol (B) and at δ = 2.21 ppm (peak n) and δ = 9.80 ppm (peak o) for $-CH_3$ and -CH=0 in acetaldehyde (C) could be observed in ¹H NMR spectra. Conversely, IBVE-H₂O could also immediately react with 2-isobutanol (B) to create the relatively stable acetaldehyde diisobutyl acetal (A). It can be also seen from Figure 3 that the characteristic resonances at $\delta = 4.67$ ppm (peak i), $\delta = 3.35$ ppm (peak h), and $\delta = 1.31$ ppm (peak j) are assigned to $-CH_{-}$, $-CH_{2}_{-}$, and $-CH_{3}$ of acetaldehyde diisobutyl acetal $(CH_3-CH-(O-CH_2-CH(CH_3)_2)_2$ (A). The conversions of IBVE with reaction time at different concentrations of $AIPW_{12}O_{40}$ are shown in Figure 4(a). All the IBVE

molecules had been converted to A, B, and C in 3.8 h when concentration of $AlPW_{12}O_{40}$ was 26 mM, while complete conversion of IBVE took 10 h when concentration of AlPW₁₂O₄₀ was 6 mM. The experimental results indicate that IBVE conversion was significantly accelerated by increasing $AlPW_{12}O_{40}$ concentration in the reaction system. On the basis of ¹H NMR spectra, the molar percents of acetaldehyde diisobutyl acetal A (A%) in organic phase with reaction time at different concentrations of AlPW₁₂O₄₀ are given in Figure 4(b). It can be seen from Figure 4(b) that all the A% was less than 100% since A was further decomposed to 2-isobutanol (**B**) and acetaldehyde (**C**) in the presence of $AlPW_{12}O_{40}$ in aqueous medium according to the Ref. 22. When $AlPW_{12}O_{40}$ concentration was 26 mM, A% was 40% within 2 h and then decreased to 3% after prolonging reaction time to 4.3 h. The similar results obtained at AlPW₁₂O₄₀ concentrations of 15 mM and 6 mM were shown in Figure 4(b). The formation of adduct (A) in the presence of $AIPW_{12}O_{40}$ in water was elucidated in Scheme 1.

The cationic polymerization of IBVE in aqueous medium was also conducted with $IBVE-HCl/AIPW_{12}O_4$ initiating system.



SCHEME 1 Possible mechanism for reaction of IBVE in aqueous medium catalyzed by AIPW₁₂O₄.



FIGURE 5 ¹H NMR spectra of IBVE–HCl and the organic mixtures after IBVE–HCl was added into water containing $AIPW_{12}O_{40}$. IBVE–HCl = 1 mL, $[AIPW_{12}O_{40}] = 26$ mM in water. $H_2O = 1$ mL.

However, no polymer could be obtained as well. The possible reason for no polymerization of IBVE in aqueous medium was that the sensitive C-Cl dormant bond of CH₃-CH(Oi-Bu)Cl reacted with water to form hemiacetal and then the unstable hemiacetal decomposed to form 2-isobutanol (B) and acetaldehyde (C) in the presence of $AIPW_{12}O_{40}$, which is similar to the results reported by Sawamoto et al.^{6(a)} To confirm the hydrolysis of IBVE-HCl adduct, IBVE-HCl adduct was added into water in the presence of $AIPW_{12}O_{40}$. ¹H NMR spectra of IBVE-HCl and the organic mixtures after IBVE-HCl was added into water containing $AlPW_{12}O_{40}$ for 10 min are given in Figure 5. The characteristic resonances at $\delta = 0.93$ ppm (peak p), $\delta = 1.89$ ppm (peak q), and $\delta =$ 3.23, 3.67 ppm (peak r) are assigned to isobutyl group of IBVE-HCl. It can be clearly observed that the characteristic resonances at $\delta = 5.71$ ppm (peak s) for -CHCl- and at δ = 1.79 ppm (peak t) for CH_3 -CHCl- in IBVE-HCl disappeared after IBVE-HCl mixed with water for 10 min in the presence of AlPW₁₂O₄₀. The characteristic resonances of the organic mixture for compounds of acetaldehyde diisobutyl acetal (A), isobutanol (B), and acetaldehyde (C) are generated in Figure 5. Therefore, it can be concluded that IBVE-HCl was rapidly hydrolyzed in water in the presence of AlPW₁₂O₄₀, leading to formation of IBVE-H₂O and acetaldehyde diisobutyl acetal (A), and then decomposed to isobutanol (B) and acetaldehyde (C). Very importantly, it can be recognized that hydrolysis of IBVE-HCl resulted in formation of HCl.

To decrease or even suppress the hydrolysis of IBVE-HCl and to induce the cationic polymerization by IBVE-HCl in

conjunction with $AIPW_{12}O_{40}$, a large amount of HCl ([HCl] = 3.56 M) was introduced into the aqueous medium. As expected, the cationic polymerization of IBVE coinitiated by $AlPW_{12}O_{40}$ could be achieved in aqueous medium at 0 $^\circ\text{C}$ in the presence of HCl. The influence of polymerization time on poly(IBVE) yield, number average molecular weight (M_n) , and MWD (M_w/M_n) and the first-order kinetic plot (insert) is shown in Figure 6. It can be seen from Figure 6 that cationic polymerization of IBVE proceeded extremely rapidly and reached polymer yield of 62% within 30 s. The addition reaction of HCl with IBVE occurred immediately to form IBVE-HCl adduct and hydrolysis of IBVE-HCl was decreased or even suppressed in the presence of a large amount of HCl. Then, IBVE-HCl formed in situ could be used as an initiator in conjunction with $AlPW_{12}O_{40}$ to induce the cationic polymerization of IBVE in aqueous medium. The polymerization was first order with respect to IBVE concentration within 20 s and the apparent constant of propagation rate $(k_{\rm p}^{\rm A})$ was determined to be 0.0503 s⁻¹. The number average molecular weights and MWDs of the resulting poly(IBVE) polymers were almost independent on polymerization time.

The cationic polymerization of IBVE coinitiated by $AIPW_{12}O_{40}$ in aqueous medium was further conducted at different concentrations of HCl, and the ¹H NMR characterization on the reaction mixtures in organic phases is presented in Figure 7. It can be found that IBVE was consumed completely and the products in organic phases were the mixtures of poly(IBVE), acetaldehyde diisobutyl acetal (**A**), isobutanol (**B**), and acetaldehyde (**C**). The cationic polymerization proceeded accompanied with side reactions, such as hydrolysis



FIGURE 6 Effect of polymerization time on polymer yield, M_n and M_w/M_n and first-order kinetic plot (insert) for cationic polymerization of IBVE coinitiated by AIPW₁₂O₄₀ in aqueous medium in the presence of HCI at 0 °C. IBVE = 3.85 mmol, [AIPW₁₂O₄₀] = 2.6 mM, [HCI]= 3.56 M.



FIGURE 7 ¹H NMR spectra of organic mixtures of poly(IBVE), IBVE–H₂O (**A**), isobutanol (**B**) and acetaldehyde (**C**) at different concentrations of HCl at 0 °C. IBVE = 3.85 mmol [AIPW₁₂O₄₀] = 2.6 mM, t = 5 min.



FIGURE 8 Effect of HCI concentration on poly(IBVE) yield and molar percent of IBVE–H₂O (C_A %) (a) and GPC traces of the corresponding poly(IBVE) products obtained at different HCI concentrations (b). IBVE = 3.85 mmol, [AIPW₁₂O₄₀] = 2.6 mM, T = 0 °C, t = 5 min.

of some IBVE-HCl to form acetaldehyde diisobutyl acetal (A) and then partial decomposition of (A) to create isobutanol (B) and acetaldehyde (C) in the presence of $AlPW_{12}O_{40}$. Effect of HCl concentration on poly(IBVE) yield and molar percent of acetaldehyde diisobutyl acetal (A) (C_A %) and GPC traces of the corresponding poly(IBVE) products obtained at different HCl concentrations are given in Figure 8. It can be clearly observed that no polymer could be obtained at HCl concentration of 0.94 M while the poly(IBVE) yield increased from 10% to 83% and C_A % in organic mixtures decreased from 42.0% to 1.2% with increasing concentration of HCl in water from 1.6 M to 6.3 M. Therefore, the hydrolysis of some IBVE-HCl in the presence of AlPW₁₂O₄₀ could be effectively decreased by increasing HCl concentration, leading to improvements in polymerization and polymer yield. As shown in Figure 8, all the GPC traces of the resulting poly(IBVE)s at four different concentrations of HCl exhibit monomodal molecular weight distributions. The number average molecular weight (M_n) of poly(IBVE) increased from 1200 to 4500 g mol⁻¹, MWD became broader and polydispersity index (M_w/M_n) increased from 2.3 to 4.4 with increasing HCl concentration from 2.2 M to 7.8 M. These results further support that cationic polymerization of IBVE in aqueous medium could be accelerated by increasing HCl concentration in reaction system. HCl played very important roles in reacting with IBVE to form IBVE-HCl initiator, and conversely, in decreasing or even suppressing the hydrolysis of C-Cl bond in IBVE-HCl and poly(IBVE) chain ends. The hydrolysis of initiating species IBVE-HCl should be prevented prior to polymerization by increasing the concentration of HCl in the presence of large amount of water. A large amount of HCl was also needed to decrease the termination of the resulting poly(IBVE) propagating species via route B during polymerization in the presence of a large amount of water (medium). Therefore, the large amount of HCl is needed to suppress the initial hydrolysis of the initiating species IBVE-HCl and to promote IBVE polymerization in

aqueous medium as well, leading to increases in polymer yield and molecular weight of polymer.

Conversely, $AIPW_{12}O_{40}$ was considered as a coinitiator to generate initiating species to induce cationic polymerization of IBVE in aqueous medium containing a large amount of HCl as no polymer could be obtained without $AIPW_{12}O_{40}$ in the control experiment at high HCl concentration of 5 M within 10 min. The result is similar to the previous report in which CH3-CH(OiBu)Cl alone did not induce polymerizations at all or polymerization of IBVE by dry HCl gas in hexane or toluene at $-40\ ^\circ C$ did not proceed. $^{6(a),17(b)}$ Effect of concentration of $AlPW_{12}O_{40}$ on cationic polymerization of IBVE in aqueous medium in the presence of sufficient amount of HCl ([HCl] = 5M) at 0 $^{\circ}$ C was investigated. Interestingly, the cationic polymerization of IBVE in aqueous medium could be induced even at very low AlPW₁₂O₄₀ concentration of 0.3 mM with polymer yield of 54% within 10 min and accelerated to 95% of polymer yield by increasing [AlPW₁₂O₄₀] to 3 mM, which was far less than that of $Ln(OTf)_3$ ([$Ln(OTf)_3$] = 150 or 300 mM) in the cationic polymerizations of IBVE or *p*MOS in aqueous medium.⁶ The molecular weight slightly increased from 3300 to 3700 g mol^{-1} with increasing $\text{AlPW}_{12}\text{O}_{40}$ concentration from 0.3 to 3 mM.

The chemical structures of head or terminal groups and stereoregularity of the resulting poly(IBVE) chains obtained via cationic polymerization of IBVE coinitiated by $AlPW_{12}O_{40}$ in aqueous medium containing sufficient amount of HCl was examined by ¹H and ¹³C NMR spectroscopy. The representative spectra of poly(IBVE) are given in Figure 9. Poly(IBVE) with $-CH_3$ head group ($\delta = 1.15$ ppm, peak 1) indicating that the cationic polymerization of IBVE was initiated from IBVE-HCl adduct. The growing polymer chain could not be terminated by adding CH₃OH as the characteristic resonance at ($\delta = 4.56$ ppm (peak 7) for -CH-O- terminal group was undetectable, which is different from that in poly(IBVE)



FIGURE 9 ¹H and ¹³C NMR spectra of ploy(IBVE) (P₆) obtained in aqueous medium at 0 °C.

obtained via cationic polymerization in organic solvent (CH₂Cl₂). All the growing polymer chains were terminated by water to create -CH2-CH(OiBu)OH terminal group. However, the unstable --CH2--CH(OiBu)OH terminal group was immediately transferred to -CH2-CH=0 aldehyde terminal group by elimination of 2-isobutanol and further to -CH=CH-CH=O alkenal terminal group by elimination of another 2-isobutanol from aldehyde terminal group.^{20,21} Therefore, poly(IBVE)s with terminal groups containing 76% of $-CH_2-CH=0$ (δ =9.81 ppm, peak 10) and 24% of -CH=CH-CH=0 (δ = 9.5 ppm, peak 16) could be obtained via cationic polymerization of IBVE coinitiated by AlPW₁₂O₄₀ in aqueous medium. It can be determined from ¹³C NMR analysis that poly(IBVE) chains with 60% of meso diad (m) could be obtained via cationic polymerization of IBVE in aqueous medium containing sufficient amount of HCl, which is similar to that in poly(IBVE) obtained via cationic polymerization of IBVE coinitiated in CH_2Cl_2 (shown in Fig. 2).

On the basis of the above observations and experimental results, a possible mechanism of cationic polymerization of IBVE coinitiated by AlPW12O40 in aqueous medium containing a sufficient amount of HCl was proposed, as shown in Scheme 2. IBVE-HCl adduct first formed by addition reaction of IBVE with HCl. The hydrolysis of IBVE-HCl in the presence of AlPW₁₂O₄₀ via route A could be effectively decreased by introduction of a sufficient amount of HCl. In the presence of a sufficient amount of HCl, the initiating species was formed from IBVE-HCl in conjunction with AlPW₁₂O₄₀ to induce cationic polymerization of IBVE via route B. A large amount of HCl was needed to promote the polymerization coinitiated by AlPW₁₂O₄₀ and to decrease the hydrolysis of IBVE-HCl catalyzed by AlPW₁₂O₄₀. The initiation, propagation, and termination of IBVE polymerization proceeded at the interface between organic IBVE droplet and aqueous phase containing AlPW12O40 and HCl. The cationic polymerization of IBVE coinitiated by $AlPW_{12}O_{40}$ in aqueous medium

containing a sufficient amount of HCl was terminated by H_2O in aqueous phase and both aldehyde and alkenal terminal groups existed in poly(IBVE) chains via elimination of 2-isobutanol.

As well known, polymerization temperature (T) is a critical factor in cationic polymerization. To examine the effect of polymerization temperature, cationic polymerizations of IBVE coinitiated with $AlPW_{12}O_{40}$ were conducted at various temperatures ranging from 0 to 50 °C. The polymer yield decreased from 63% to 21% and M_n of poly(IBVE) decreased from 4500 to 1800 g mol⁻¹ with increasing temperature from 0 to 50 °C. Higher temperature might accelerate the side reactions, such as chain transfer and termination. The inverse effect of polymerization temperature on molecular weight has been quantitatively expressed by Arrhenius equation, that is, $\ln M_{\rm n} = \ln A - \Delta E/RT^{23-25}$ The overall activation energy difference (ΔE or $E_{\rm DP}$) was calculated to be -13.5 kJ mol⁻¹ from the slope of the linear Arrhenius plot of $\ln(M_n)$ versus 1/T for the temperature interval from 0 to 50 °C, shown in Figure 10.

Cationic Polymerization of IBVE Coinitiated by $H_3PW_{12}O_{40}$ and its Salts in Aqueous Medium

A series of heteropolyacid and its salts, such as $H_3PW_{12}O_{40}$, AlPW₁₂O₄₀, FePW₁₂O₄₀, K₃PW₁₂O₄₀, or Na₃PW₁₂O₄₀, were used as coinitiators for the cationic polymerizations of IBVE in aqueous medium containing a large amount of HCl ([HCl]= 4 M and 6 M). The polymer yield, M_n , and polydispersity index (M_w/M_n) of poly(IBVE)s obtained by $H_3PW_{12}O_{40}$ and it salts are presented in Figure 11. The experimental results illustrate that all heteropolyacid $H_3PW_{12}O_{40}$ and its salts were efficient to coinitiate the cationic polymerization of IBVE in aqueous medium, in which polymer yield could reach about 80% by using $H_3PW_{12}O_{40}$ or AlPW₁₂O₄₀ as a coinitiator at [HCl] = 6 M. The number average molecular weights of the resulting poly(IBVE)s



SCHEME 2 Possible mechanism of cationic polymerization of IBVE coinitiated by AIPW₁₂O₄₀ in aqueous medium containing a sufficient amount of HCI.

obtained in aqueous medium were in the range of 2000–3800 g mol⁻¹, and the polydispersity indexes of polymers kept at around 3.0, which are closed to those of polymers obtained in organic solvent CH_2Cl_2 . We proposed the similar results were due to the same $PW_{12}O_{40}^{3-}$ anion in the polymerization system with a sufficient amount of HCl.

EXPERIMENTAL

Materials

IBVE (98%, Aldrich) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight by potassium hydroxide, and distilled twice from calcium hydride (CaH₂) before use. Dichloromethane (CH₂Cl₂; AR; Beijing Yili Fine Chemical Co.), *n*-hexane (*n*-Hex; AR.; Beijing Yili Fine Chemical Co.), and THF (AR; Beijing Yili Fine Chemical Co.) were distilled from CaH₂ before use as described previously.²⁶ Dodecatungstophosphoric acid hydrate (H₃PW₁₂O₄₀·*n*H₂O; AR., Aldrich, H₂O = 6 wt %), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O; AR, Beijing Chemical Co.), sodium carbonate (Na₂CO₃; AR; Beijing Chemical Co.), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O; AR; Beijing Chemical Co.), and methanol (MeOH; AR; Beijing Yili Fine Chemical Co.) were used as received.

Procedures

Aluminum dodecatungstophosphate ($AIPW_{12}O_{40}$), iron dodecatungstophosphate ($FePW_{12}O_{40}$), potassium dodeca-

tungstophosphate ($K_3PW_{12}O_{40}$), sodium dodecatungstophosphate ($Na_3PW_{12}O_{40}$) were synthesized with quantitative yields by reaction of $H_3PW_{12}O_{40}$ with $Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, K_2CO_3 , or Na_2CO_3 aqueous solution, respectively.²⁷ IBVE-HCl adduct was synthesized by bubbling dry HCl gas through a solution of IBVE in hexane (1.0 M) at 0 °C.²⁰ HCl was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it



FIGURE 10 Arrhenius plot of $In(M_n)$ versus 1/T for IBVE polymerization in aqueous medium.



FIGURE 11 Cationic polymerization of IBVE coinitiated by various heteropolyacid and its salts in aqueous medium. IBVE = 3.85 mmol, t = 5 min, $T = 0 \circ C$, [heteropolyacid/salts] = 2.6 mM.

time.

nal standard ($\delta_{\rm H} = 0.00$).

through a column packed with calcium chloride. After 30 min, excess HCl in solution was removed by bubbling dry nitrogen at 0 °C for 30 min, and the clean and quantitative formation of IBVE-HCl adduct was confirmed by ¹H NMR spectroscopy.

Polymerizations

All the polymerization reactions were carried out under a nitrogen atmosphere in glass tubes. A typical cationic polymerization of IBVE in aqueous medium (water) was conducted as follows: $\mbox{AlPW}_{12}\mbox{O}_{40}$ was dissolved in water, and then HCl aqueous was added. The neat monomer IBVE (0.5 mL; 3.85 mmol) was added into the above aqueous phase (3.0 mL) to start the polymerization. The polymerization was carried out under thermal regulation (typically at 0 °C) with severe magnetical stirring at speed of around 300 rpm. After predetermined time, 1 mL of methanol was injected to terminate the polymerization and 5 mL CH₂Cl₂ was added in to dissolve the resulting poly(IBVE). Organic phase was separated, transferred, and evaporated to obtain poly(IBVE) products. A typical cationic polymerization of IBVE in CH₂Cl₂ was carried out as follows: IBVE solution in CH₂Cl₂ (2 mL, 1 M) and IBVE-HCl solution in hexane (0.05 mL, 1 M) were successively introduced into polymerization reactor with $AlPW_{12}O_{40}$ at 0 $\,^\circ\text{C}$ under magnetic stirring. After predetermined time, 1 mL of methanol was injected to terminate polymerization. Poly(IBVE) was obtained by removing residue catalyst via centrifugation and evaporating organic solvents. The resulting poly(IBVE) was dried in a vacuum oven at 40 °C to a constant weight. Poly(IBVE) yield was determined gravimetrically.

Characterization

Number average molecular weight (M_n) , weight average molecular weight (M_w) , and MWD (M_w/M_n) of poly(IBVE) were determined with a Waters 515-2410 GPC system equipped with four Waters styragel columns connected in the following series: 500, 10^3 , 10^4 , and 10^5 at 30 °C. THF served as solvent, poly(IBVE) with a concentration of 20 mg of poly(-IBVE)/10 mL of THF, and THF was also used as mobile phase at a flow rate of 1.0 mL min $^{-1}$. The calibration of molecular weight was based on polystyrene standards. NMR characterization of the reaction mixtures and poly(IBVE) was performed on a Bruker AV400 MHz spectrometer using

 $A\% = \frac{S_{\rm A}}{S_{\rm IBVE0}/6 - S_{\rm IBVEt}} \times 100$ Concentration of acetaldehyde diisobutyl acetal (A, C_A %) is

CDCl₃ as a solvent at 25 °C. ¹H NMR spectra of sample solutions in CDCl₃ were calibrated to tetramethylsilane as inter-

Percent of acetaldehyde diisobutyl acetal (A%) is defined as

the ratio of acetaldehyde diisobutyl acetal (A) in the products from IBVE in aqueous medium in the presence of

AlPW₁₂O₄₀ according to eq 1. S_A is the integral value of

around 4.67 ppm of acetaldehyde diisobutyl acetal. S_{IBVE0} is

the integral value of around 0.92 ppm of initial IBVE and S_{IB} .

VEt is the integral value of around 6.49 ppm for a period of

defined as the molar ratio of acetaldehyde diisobutyl acetal A to original IBVE in the reaction mixture according to eq 2.

$$C_{\rm A}\% = \frac{S_{\rm A}}{S_{\rm IBVE0}/6} \times 100 \tag{2}$$

(1)

CONCLUSIONS

Suspension cationic polymerization of IBVE coinitiated by $H_3PW_{12}O_{40}$, $AlPW_{12}O_{40}$, $FePW_{12}O_{40}$, $K_3PW_{12}O_{40}$, or $Na_3PW_{12}O_{40}$ in aqueous medium could be achieved up to more than 83% of poly(IBVE) yield in the presence of a large amount of HCl. The number average molecular weights of the resulting isotactic-rich poly(IBVE)s with m diad of 60% obtained in aqueous medium were in the range of $1200-4500 \text{ g mol}^{-1}$ and the polydispersity indexes of polymers kept at around 3.0, which are similar to those of polymers obtained in organic solvent CH₂Cl₂. A sufficient amount of HCl ([HCl] > 1.6 M) was needed to decrease or suppress the hydrolysis of initiator IBVE-HCl and to accelerate the cationic polymerization of IBVE in aqueous medium. The cationic polymerization of IBVE in aqueous medium in the presence of HCl proceeded extremely rapidly with apparent constant of propagation rate (k_n^A) of 0.0503 s⁻¹. The yield and molecular weight of poly(IBVE) could be increased by increasing the amount of HCl and AlPW₁₂O₄₀ concentration or by decreasing polymerization temperature. The elementary reactions for the cationic polymerization, including initiation, propagation, and

termination happened at the interface between IBVE droplet and aqueous phase. All the poly(IBVE) growing chains were terminated by H_2O and further transferred to aldehyde and alkenal terminal groups in polymer chains by elimination of 2-isobutanol.

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REFERENCES AND NOTES

1 (a) J. P. Kennedy, B. Iván, Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice; Hanser: Munich, Germany, **1991**; (b) K. Matyjaszewski, M. Sawamoto, In Cationic Polymerizations: Mechanism, Synthesis, and Applications; K. Matyjaszewski, Ed.; Marcel Dekker: New York, **1996**; (c) M. Sawamoto, *Prog. Polym. Sci.* **1991**, *16*, 111–172; (d) S. Aoshima, S. Kanaoka, *Chem. Rev.* **2009**, *109*, 5245–5287; (e) A. Kanazawa, S. Kanaoka, S. Aoshima, *Macromolecules* **2009**, *42*, 3965–3972; (f) I. M. Zaleska, M. Kitagawa, S. Sugihara, I. Ikeda, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5169–5179; (g) S. Sugihara, M. Kitagawa, Y. Inagawa, I. M. Zaleska, I. Ikeda, *Polym. Bull.* **2010**, *64*, 209–220.

2 S. V. Kostjuk, F. Ganachaud, *Acc. Chem. Res.* **2009**, *43*, 357–367.

3 (a) K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 5405–5410; (b) K. Satoh, J. Nakashima, M. Kamigaito, M. Sawamoto, *Macromolecules* **2001**, *34*, 396–401.

4 A. V. Radchenko, S. V. Kostjuk, I. V. Vasilenko, F. Ganachaud, F. N. Kaputsky, *Eur. Polym. J.* **2007**, *43*, 2576–2583; (b) A. V. Radchenko, S. V. Kostjuk, L. V. Gaponik, *Polym. Bull.* **2011**, *65*, 1–12.

5 S. Cauvin, F. Ganachaud, M. Moreau, P. Hemery, *Chem. Commun.* 2005, 2713–2715.

6 (a) K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 3827–3832; (b) K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 4660–4666; (c) K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 5836–5840; (d) K. Satoh, M. Kamigaito, M. Sawamoto, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *38*, 2728–2733.

7 V. Touchard, C. Graillat, C. Boisson, F. D'Agosto, R. Spitz, *Macromolecules* 2004, *37*, 3136–3142.

8 M. U. Kahveci, M. A. Tasdelen, W. D. Cook, Y. Yagci, *Macro*mol. Chem. Phys. 2008, 209, 1881–1886.

9 (a) S. Cauvin, A. Sadoun, R. Dos Santos, J. Belleney, F. Ganachaud, P. Hemery, *Macromolecules* 2002, *35*, 7919–7927; (b) S. Cauvin, F. Ganachaud, V. Touchard, P. Hemery, F. Leising, *Macromolecules* 2004, *37*, 3214–3221.

10 S. V. Kostjuk, F. Ganachaud, *Macromolecules* **2006**, *39*, 3110–3113; (b) S. V. Kostjuk, A. V. Radchenko, F. Ganachaud, *Macromolecules* **2007**, *40*, 482–490; (c) S. V. Kostjuk, A. V. Radchenko, F. Ganachaud, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4734–4747; (d) S. V. Kostjuk, S. Ouardad, F. Peruch,

A. Deffieux, C. Absalon, J. E. Puskas, F. Ganachaud, *Macromolecules* **2011**, *44*, 1372–1384.

11 (a) S. P. Lewis, N. J. Taylor, W. E. Piers, S. Collins, *J. Am. Chem. Soc.* **2003**, *125*, 14686–14687; (b) S. P. Lewis, L. D. Henderson, B. D. Chandler, M. Parvez, W. E. Piers, S. Collins, *J. Am. Chem. Soc.* **2005**, *127*, 46–47; (c) J. Chai, S. P. Lewis, S. Collins, T. J. J. Sciarone, L. D. Henderson, P. A. Chase, G. J. Irvine, W. E. Piers, M. R. J. Elsegood, W. Clegg, *Organometallics* **2007**, *26*, 5667–5679; (d) S. P. Lewis, J. Chai, S. Collins, T. J. J. Sciarone, L. D. Henderson, C. Fan, M. Parvez, W. E. Piers, *Organometallics* **2009**, *28*, 249–263.

12 (a) A. Zhang, G. Zhang, H. Zhang, *J. Appl. Polym. Sci.* **1999**, *73*, 2303–2308; (b) Y. Chen, G. Zhang, H. Zhang, *J. Appl. Polym. Sci.* **2001**, *82*, 269–275.

13 I. V. Kozhevnikov, Chem. Rev. 1998, 98, 171-198.

14 T. Okuhara, Chem. Rev. 2002, 102, 3641–3666.

15 (a) D. Chen, Z. Xue, Z. Su, *J. Mol. Catal. A: Chem.* **2004**, *208*, 91–95; (b) D. Chen, Z. Xue, Z. Su, *J. Mol. Catal. A: Chem.* **2003**, *203*, 307–312.

16 A. Aouissi, Z. A. Al-Othman, H Al-Anezi, *Molecules* **2010**, *15*, 3319–3328.

17 (a) Y. Matsuo, S. Kanaoka, S. Aoshima, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2009**, *50*, 157; (b) S. Sugihara, Y. Tanabe, M. Kitagawa, I. Ikeda, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 1913–1918; (c) Y. Matsuo, S. Kanaoka, S. Aoshima, *Kobunshi Ronbunshu*, **2011**, *68*, 176–181.

18 J. D. Burrington, J. R. Johnson, J. K. Pudelski, *Top. Catal.* **2003**, *23*, 175–181.

19 (a) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, *Tetrahedron Lett.* **2003**, *44*, 3951–3954; (b) H. Firouzabadi, N. Iranpoor, F. Nowrouzi, *Tetrahedron* **2004**, *60*, 10843–10850; (c) H. Firouzabadi, N. Iranpoor, A. A. Jafari, *Tetrahedron Lett.* **2005**, *46*, 2683–2686; (d) H. Firouzabadi, N. Iranpoor, A. Khoshnood, *Catal. Commun.* **2008**, *9*, 529–553.

20 H. Katayama, M. Kamigaito, M. Sawamoto, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1249–1257.

21 A. Kanazawa, S. Kanaoka, S. Aoshima, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 3702–3708.

22 L. G. Wade, Organic Chemistry; Chemical Industry Press: Beijing, 2005, p 746.

23 R. M. Thomas, W. J. Sparks, P. K. Frolich, M. Otto, M. Muller-Cunradi, *J. Am. Chem. Soc.* **1940**, *62*, 276–280.

24 P. J. Flory, Principles of Polymer Chemistry; Cornell University Press: Ithaca, New York, 1953, pp 218.

25 (a) J. P. Kennedy, Cationic Polymerization of Olefins: A Critical Inventory; Wiley Interscience: New York, **1975**. (b) J. P. Kennedy, E. Marechal, Carbocationic Polymerization; Wiley Interscience: New York, **1982**.

26 (a) Y. Li, Y. X. Wu, X. Xu, L. Liang, G. Wu, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3053–3061; (b) Q. Liu, Y. X. Wu; Y. Zhang, P. F. Yan, R. W. Xu, *Polymer* **2010**, *51*, 5960–5969; (c) Q. Liu, Y. X. Wu, P. F. Yan, Y. Zhang, R. W. Xu, *Macromolecules* **2011**, *44*, 1866–1875.

27 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 1983, *22*, 207–216.