Supporting Information

Title: Cationic Polymerization of Isobutyl Vinyl Ether in an Imidazole-

Based Ionic Liquid: Characteristics and Mechanism

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Figure 1 Kinetic plots of IBVE polymerization in dichloromethane by addition bases: (A)conversion vs. time; (B) $\ln([M_0]/[M])$ vs. time; (C) M_n and M_w/M_n vs. conversion. [TiCl₄]=0.048. [IBVE-HCl]=0.003M, [IBVE]=0.97M, [added base] =0.05M, *T*=0 °C.



Cationic polymerization of IBVE was examined in the absence or presence of an added bases, ethyl acetate and 1,4-dioxane, in dichloromethane at 0°C. Polymerization

in the presence of ethyl acetate or 1,4-dioxane showed quite different behavior compared to that without a base in dichloromethane system. The linear first-order plots showed that the concentration of growing centers remained constant. The absence of termination also confirmed the living nature of the polymerization. The M_n increased in direct proportion to the monomer conversion with narrow MWDs.

Figure 2 the effects of DTBP concentration on conversion, reaction rate, and M_n and polydispersity: (A)conversion vs. time; (B) ln([M0]/[M]) vs. time; (C) M_n and M_w/M_n vs. conversion;(D) Representative GPC curve of poly(IBVE)s.[TiCl₄]=0.048, [IBVE-HCl]=0.003M, [IBVE]=0.97M, *T*=0 °C.





As shown in Figure 2B, the first-order plots of $\ln([M_0]/[M])$ versus time are linear. We used initial slopes of these plots to calculate the apparent rate constants. It is clearly indicated that the polymerization rate decreases did not change significantly

with DTBP concentration. Also, it was found that there was no significant effect of DTBP concentration on M_n and M_w/M_n values. So DTBP was only effective for suppression of the uncontrolled portion, did not affect on carboncation.