

Living cationic polymerization of poly (isobutyl vinyl ether) and PVA derived therefrom

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Abstract

Some new synthetic routes for the preparation of poly (isobutyl vinyl ether) (P(IBVE)) having a controllable molar mass with narrow distribution via catalytic or photoinduced living cationic polymerization and their conversion to corresponding PVA have been developed. It was found that the combination of iodomethyl methyl ether (IMME)-zinc iodide is effective in the initiation of the catalytic and the various combinations of diphenyliodonium halides, well known photocationic initiators (DPIX) with zinc halides (ZnX_2) are also useful in photoinduced living cationic polymerization of isobutyl vinyl ether (IBVE). Polymerization both in the catalytic and photoinduced systems precede until the full consumption of the monomer and the rate of polymerization increases as the concentration of the catalyst or photoinitiator. The number average molar mass of the resulting polymer is proportional with % conversion, which is determined by the ratio of monomer consumed and the initial values of the catalyst or initiator. The living nature was also confirmed by subsequent monomer addition technique.

Introduction

Molecular design of the polymers, such as control of the molar mass and its distribution of the polymer and the introduction of the appropriate functional groups to the end of polymers via living polymer system have been one of the utmost important subjects to many polymer chemists. Although much progress in anionic living polymer systems has been made (1), living polymer systems via cationic mechanism has been delayed due to the difficulty in obtaining stable cationic species (2). Recently, several attempts have been reported that living cationic P(IBVE) has been realized via adduct of monomer and protonic acid (3). In this article, we report some living cationic polymer systems of poly (isobutyl vinyl ether), initiated by IMME, a new type catalyst or photoinduced system in the presence of DPIX.

This, therefore provides an new synthetic way to prepare poly vinyl alcohol (PVA) having controlled molar mass with narrow molar mass by hydrolysis of corresponding P(IBVE).

Experimental

IBVE, monomer, solvents (toluene or methylene chloride) were purified by conventional distillation method. IMME, DPIX of reagent grade were used without further purification. Polymerization samples were prepared on a high vacuum system without contacting with air. Photoirradiation for the samples for photoinduced polymerization was carried out at -78°C for 10 min in order to prevent the polymerization during the irradiation using a high pressure Hg lamp was used in photoirradiation. Polymerization ampoules were allowed to stand in the dark for the polymerization under various temperatures after photoirradiation. % conversion was determined by gravimetry and molar mass and distribution were determined by GPC(Spectra-Physics SP 8430).

Results and discussion

Time-conversion curve of the system initiated by IMME- ZnI_2 , carried out several temperatures is shown in Fig. 1, demonstrating that % conversion reaches almost 100% in most cases. However, the linear dependence of number average molar mass on % conversion, a strong evidence of the living nature of the system is only recognized when the reaction temperature is kept below 0°C . This indicates that the processes other than propagation such as termination or chain transfer is absent in this system when temperature is kept below 0°C as shown in Fig. 2.

Fig. 3 and 4 show time-conversion curves and the dependence of the molar mass of the resulting polymer in the photoinduced cationic polymerization of IBVE carried out in the presence of various combinations of DPIX- ZnX_2 in methylene chloride, respectively, indicating that living nature is appeared only in the case when reaction temperature is kept below -30°C ,

irregardless of the halide anion of the initiator or zinc halide, however, a severe loss of living nature was appeared when zinc chloride is used. The best living nature is always observed when the combination of diphenyliodonium iodide (DPII) – ZnI₂ is used. It was also found that the living nature is appeared in the polymerization, carried out in toluene, a non-polar solvent, in the presence of DPII-ZnI₂ even at relatively higher temperature than 0 °C. The molar mass distribution of the polymer is always less than 1.3. The effect of solvent polarity and temperature on the living nature, and the preparation of PVA from P(IBVE) were also discussed.

Conclusions

Living nature of cationic P(IBVE), prepared in the presence of IMME-ZnI₂ and photoinduced in the presence of DPII-ZnX₂ has been investigated. It was found that P(IBVE) having various molar mass with narrow distribution is easily obtainable by adjusting the molar ratio of monomer and the catalyst or photoinitiator. This makes it possible to prepare high molar mass PVA with narrow distribution (whose number average degree of polymerization is larger than 7000) by hydrolysis of corresponding P(IBVE) using Lewis acid, such as BCl₃

References

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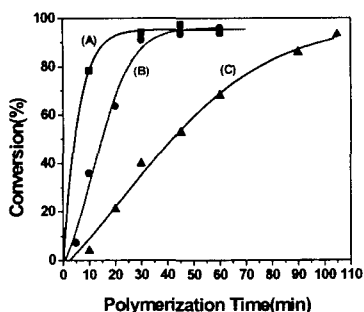


Fig. 1 Time-conversion curves of IBVE initiated by IMME-ZnI₂ in toluene/DEE 9/1(v/v) mixed solvent. Temp: 0 °C, [M]= 1.6M, [IMME]=4.9mM, [ZnI₂]=0.167mM.

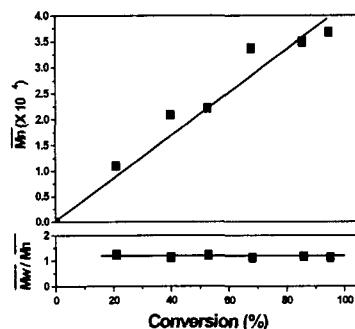


Fig.2 Dependence of Mn on % conversion. Conditions are same with those given in Fig. 1.

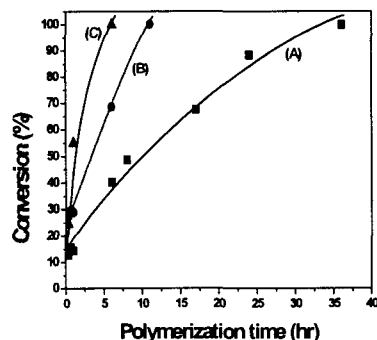


Fig. 3 Time-conversion curves of IBVE polymerization, photoinduced in the presence of DPII and ZnI₂ in toluene-DEE mixed solvent at various temperatures. [M] =1.42M, [ZnI₂]= 1.16mM, [DPII]=0.907mM, temp: (A)=-30 °C, (B)=-15 °C, (C)=0 °C.

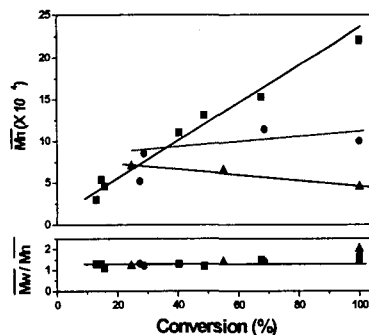


Fig. 4. Dependence of Mn on % conversion in the photoinduced IBVE polymerization. Conditions are same with those given in Fig. 3.