

Additive Effects in Living Cationic Polymerization of tert-Butyl Vinyl Ether, initiated by Iodine

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Abstract

Living nature was appeared in the cationic polymerization of tert-butyl vinyl ether (TBVE), initiated by iodine, carried out in toluene at -78°C . It was found that the number average molar mass of the resulting polymer (\overline{M}_n) increases linearly as the conversion to polymer increase which reveals that there is no operation of chain transfer or termination process in this system. The polymers having narrow distribution and having molar mass of the resulting polymers are dependent on molar ratio of monomer and iodine.

Introduction

Although, several reports regarding on the cationic polymerization of TBVE, there is no one describes the living nature, we report some of our recent findings concerning the improvement of living nature of cationic polymerization of tert-butyl vinyl ether (TBVE) initiated by iodine.

Experimental

Samples for polymerization were prepared by trap-to-trap distillation of TBVE and toluene where iodine and additive were placed on a vacuum line. The ampoule was sealed off after degassing by repeated freeze-thaw cycles. Polymerization was carried out at -78°C and polymer was precipitated by the addition of small amount of ammonical methanol. Molar mass and its distribution determined by means of GPC (Spectra Physics SP8430) using tetrahydrofuran as the eluent (10^5 , 10^4 , 10^3 Å polystyrene gel columns in series. Flow rate: 1.0mL/min). Polystyrene standard was used for the calibration.

Results

Comparison of the time-conversion curves of TBVE polymerization and the dependence of number average molar mass of resulting polymer on % conversion in the absence and presence of

an additive, n-butyl ammonium iodide (nBu_4NI) clearly shows the living nature of the polymerization is significantly improved by the addition of the salt which have a common ion with that of the cationic propagating end, although the rate of polymerization decreases as shown in the Fig.

Conclusion

It was found that the living nature of cationic polymerization of TBVE could be improved by the addition of salt having a common ion.

References

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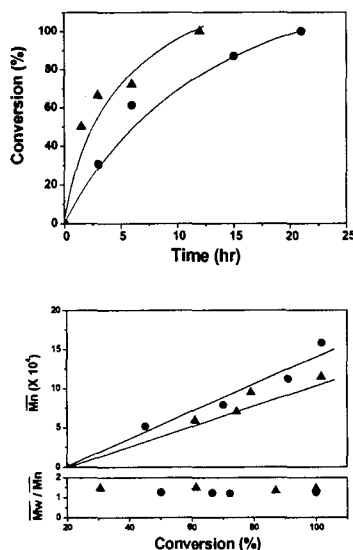


Figure 1. Effect of added nBu_4NI on TBVE polymerization in toluene at -78°C : $[\text{M}]_0 = 1.42\text{M}$; $[\text{I}_2]_0 = 1.16\text{mM}$; $[\text{ZnI}_2]_0 = 1.16\text{mM}$; $[\text{nBu}_4\text{NI}]_0 = \bullet$; 1.16mM, \blacktriangle ; 0mM.