LOW COST BIFUNCTIONAL INITIATORS FOR BIDIRECTIONAL LIVING CATIONIC POLYMERIZATION OF ISOBUTYLENE AND THEIR APPLICATIONS

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ABSTRACT

The discovery of living isobutylene (IB) polymerization was a critical event in synthetic polymer science since it has led to a host of new useful materials, including telechelic intermediates. The key to these developments was the initiating system that afforded the synthesis of polymeric materials with precisely defined structures. The bifunctional initiator that has been employed worldwide in this field is the so-called “hindered” initiator 5-tert-butyl-1,3-bis(1-chloro-1-methyl)benzene (HDCCl) which in conjunction with TiCl₄ coinitiator virtually instantaneously induces bidirectional living olefin polymerizations. The synthesis of HDCCl, however, is expensive as it requires several steps and expensive reagents.

In this presentation we report discovery of novel low cost bifunctional initiators bis-benzocyclobutene-diol and -dichloride, (bBCB-diOH) and (bBCB-diCl) for living cationic bidirectional polymerization of olefins, e.g., IB. bBCB-diOH was quantitatively synthesized in one step by UV radiation of commercially available diacetyl durene, and bBCB-diCl by hydrochlorination of bBCB-diOH. These molecules, in conjunction with TiCl₄ coinitiator, initiate the living polymerization of IB. Livingness was demonstrated by linear conversion versus molecular weight plots and narrow molecular weight distributions. The synthesis of relatively low molecular weight (Mn <3,000 g/mol) allyl-telechelic PIB used for the synthesis of PIB-based polyurethanes, and that of relatively high molecular (Mn>30,000) living PIB telechelics for the synthesis of thermoplastic elastomers, by the use of bBCB-diCl were all conducted. It has also been found that bBCB-diCl initiator can induce the living bidirectional block copolymerization of IB followed by styrene (St) and produce PST-b-PIB-b-PSt (SIBS) triblocks. The molecular weights of the triblocks kept significantly increasing long after St conversion which reached completion during syntheses. Results were explained by the formation of blends consisting of the expected linear SIBS plus hyperbranched SIBS [HB(SIBS)ₙ]. The properties of SIBS/HB(SIBS)ₙ blends were superior to those of SIBS. The microstructure/property relationship of HB(SIBS)ₙ was discussed and the reasons for enhanced properties of SIBS/HB(SIBS)ₙ blends were analyzed. Additionally, we discovered that thermolysis of allyl-telechelic polyisobutylene, A-PIB-A produced by the bBCB-diCl initiator quantitatively converts the central bBCB fragment to a substituted conjugated tetraene, A-PIB-tetraene-PIB-A which then permits formation of useful intermediates for the synthesis of novel PIB-based materials for various end uses.