Inifers

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator Transfer Agents (Inifers)

48. Continuous Synthesis of Linear Telechelic Polyisobutylene

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Summary

The continuous polymerization technique developed earlier for the synthesis of three-arm star telechelic polyisobutenes (PIBs) has been extended and used for the preparation of linear telechelic PIBs. It is demonstrated that for a period of 6-10 residence times liquid α,ω-ditert.-chloropolyisobutenes with close to theoretical terminal functionalities, molecular weights and molecular weight distributions can readily be produced at -80°C. During the latter stages of the continuous process the polymerization tends to become heterogeneous and the molecular weights increase. The expected telechelic structure has been corroborated by conventional 1H NMR spectroscopy and by the recently developed modified Kennedy-Smith plot.

Introduction

Earlier publications in this series concerned a semi-continuous (1) and a continuous (2) polymerization technique mainly for the preparation of three-arm star telechelic polyisobutenes PIBs carrying tert.-chlorine end groups. These papers also contain kinetic expressions that describe the continuous systems, in particular the effect of reagent concentrations on molecular weights.

It has been demonstrated that virtually perfectly telechelic PIBs can be produced by these techniques with predetermined molecular weights and close to theoretical molecular weight distributions. The present publication concerns an extension and minor modification of our earlier technique, and demonstrates that α,ω-ditert.-chloro PIBs (i.e., linear telechelics) with essentially theoretical number average end group concentrations ($F_n = 2.0 \pm 0.1$) and molecular weights ($M_n = [M]_o/[I]_o$) can also be readily and conveniently synthesized. Results obtained by 1H NMR spectroscopy and by the use of the modified Kennedy-Smith plot demonstrate the compositional homogeneity of the telechelic products obtained.

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Experimental

The purification of isobutylene, BCl3, and methyl chloride together with the preparation and purification of the binifer, p-bis(α, α-dimethyl chloromethyl)benzene, have been described (3). Purification of hexane has also been described (1). Continuous experiments have been carried out in a stainless steel dry-box under a dry nitrogen atmosphere at -80°C.

Figure 1 shows the scheme of the glass assembly used. This equipment is similar to that used for the preparation of three-arm star telechelic PIBs (2) except the volume of the stirred reactor (III) has been reduced from 250 ml to 100 ml to decrease the residence time. Thus we were able to run continuous experiments for 17-20 residence times. Reservoir I (1000 ml) contained the monomer, binifer, in a CH2Cl2 : hexane (75:25 vol %) solvent mixture. Reservoir II (1000 ml) was charged with BCl3 in a CH2Cl2 : hexane (75:25) mixture. Erlenmeyer flasks (100 ml) containing ~10 ml MeOH were used as receivers (IV). The glass reservoirs and flasks were immersed in a thermostatted cooling bath at -80°C. By the use of this assembly we were able to follow every phase of the continuous process.

Figure 1. Scheme of Glass Assembly Used for Continuous Polymerization

Molecular weights were determined by a Waters high-pressure GPC instrument (Model 6000A pump). Details of our GPC methodology have been described (1). The RI and UV traces produced by the Differential Refractometer (Model 2401) and UV Absorbance Detector (Model 440), respectively, have been used to construct and calculate the modified Kennedy-Smith plot. Details of this recently developed technique have been described (4).

Results and Discussion

A) Reaction Profiles

It has been repeatedly demonstrated that mono-, di- and tri-functional telechelic polyisobutenes with close to