

Living carbocationic polymerization

LXI. Narrow molecular weight distribution polyisobutylenes prepared by esters and ketones as electron donors^{*}

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Abstract

Electron donors (EDs) effectively mediate living carbocationic polymerizations (LC⁺Pzn), for example, that of isobutylene (IB). The purpose of this research was to investigate the effect of various new EDs, specifically esters and ketones on the LC⁺Pzn of IB, and to determine the effect of these EDs on the molecular weight distribution (MWD) of polyisobutylene (PIB) under various experimental conditions. Thus the LC⁺Pzn of IB was effected by the dicumyl chloride (DCC)/SnCl₄ initiating system in the presence of various EDs, such as dimethyl phthalate, di-*n*-octyl phthalate, methyl benzoate, ethyl isobutyrate, dimethyl 3,3-dimethylglutarate, dimethyl terephthalate, dimethyl 5-*n*-butyl-isophthalate, trimethyl 1,3,5-benzenetricarboxylate and acetophenone and benzophenone, in CH₂Cl₂ at -30°C, and the \bar{M}_w/\bar{M}_n of the PIB was determined. It was found that the nature and the concentration of the ED strongly influence MWD. Under well-defined conditions in the presence of dimethyl phthalate or di-*n*-octyl phthalate, polymers with close to Poisson distribution ($\bar{M}_w/\bar{M}_n=1.03$) could be obtained.

Introduction

EDs efficiently mediate the LC⁺Pzn of IB leading to narrow MWD polymer and also reduce undesired side reactions such as indane formation and initiation by protic impurities¹⁻³. N,N-dimethylacetamide and dimethylsulfoxide are among familiar EDs for LC⁺Pzn¹⁻³. Recently other donors like amines and amides⁴, such as dimethylamine, trimethylamine, dibutylamine, pyridine and its derivatives⁵ have also been examined. Carbonyl compounds received less attention, perhaps because ethyl acetate which was the first ED examined was found to exhibit a relatively poor donor effect⁶. In contrast to ethyl acetate, we have found many carbonyl compounds, especially some aromatic carbonyls, that are excellent EDs and produce very well-defined narrow MWD products.

The purpose of these investigations was to study the effect of various hitherto unexamined esters and ketones on the LC⁺Pzn of IB, particularly on the MWD of PIBs prepared under various experimental conditions. Another objective of this work was to search for a correlation between the structure of the ED and MWD.

Experimental

Materials: Table 1 shows the chemical structures and abbreviations of the EDs used. Dimethylacetamide (DMA), methyl benzoate (MB), benzophenone (BP),

^{*} This paper is in continuation with: Polymer Bulletin, J.P. Kennedy, et al., Polymer Bulletin 23, 245 (1992).

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Gas Phase Cationic Polymerization of Unsaturated Monomers Initiated by BF₃ Leonard Forte,1989

Designed Polymers by Carbocationic Macromolecular Engineering Joseph P. Kennedy,Béla Iván,1992

Cationic Polymerization Rudolf Faust,Timothy Daniel Shaffer,1997 Cationic Polymerization covers the essential practices and latest procedures for working with carbocationic and ring opening polymerization It presents the kinetic rates of individual steps of cationic polymerization using laser flash photolysis and competitive experimental techniques It examines several new catalyst systems including a water resistant recoverable Lewis acid for ring polymerization It also highlights the use of living carbocationic techniques to prepare amphiphilic block copolymers multiarm star polymers and coupled copolymers of isobutylene and it compares the similarities and differences of living radical and carbocationic techniques Essential for chemists working with cationic polymerization the volume is also useful for researchers new to the field

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Palladium-catalyzed Polymerization of Unsaturated Monomers Daniel Haviv,1987

Process for the Preparation of Polymers from Olefinically Unsaturated Monomers L. Heider,BASF Aktiengesellschaft,1990

Quasiliving Carbocationic Polymerization Joseph Paul Kennedy,1982

The Effect of Reaction Conditions on Quasiliving Carbocationic Polymerization of Isobutylene Werner Groh Péter,2005

Carbocationic Polymerization in the Presence of Sterically Hindered Bases ,1982

From Living Carbocationic to Living Radical Polymerization ,1994 Living carbocationic polymerization is compared to living radical process Similarities and differences are discussed Living radical polymerization of vinyl acetate and methyl methacrylate to provide polymers with controlled molecular weights and narrow molecular weight distribution M_w/M_n

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