

Living carbocationic polymerization

LXI. Narrow molecular weight distribution polyisobutylenes prepared by esters and ketones as electron donors¹

Jiashi Si and J. P. Kennedy²

Materials Science Institute of Polymer Science, The University of Akron, Akron, OH 44325-3696, USA

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)/3Cl₂ initiating system in the presence of various EDs, such as dimethyl phthalate, di-*t*-octyl phthalate, methyl benzoate, ethyl isobutyrate, dimethyl 3,3-dimethylglutarate, dimethyl terephthalate, dimethyl 5-*t*-butyl-isophthalate, trimethyl 1,3,5-benzene-tricarboxylate and acetophenone and benzophenone, in CH₂Cl at -30°C, and the M_w/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-*t*-octyl phthalate, polymers with close to Poisson distribution ($M_w/M_n=1.03$) 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 impurities^{1,2}. N,N-dimethylacetamide and dimethylsulfoxide are among familiar EDs for LC⁺Pzn^{1,3}. Recently other donors like amines and anilides⁴, 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),

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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.

Synthesis and Polymerization of Metal-Containing Monomers Anatoly D. Pomogailo, 2018-01-31 This book overviews methods for the synthesis of metal containing monomers with various types of metal bonds to the organic moiety of the molecule such as ionic, covalent, donor-acceptor and others. Published data on homopolymerization, copolymerization and graft polymerization of these monomers are generalized. **Synthesis and Polymerization of Metal Containing Monomers** discusses features typical of the molecular and structural organization of the resulting metal containing polymers, their properties and the associated major applications such as catalytical and biological activity, electrophysical characteristics and thermal resistance. Polymerization and Copolymerization of Unsaturated Organotin and Related Monomers Maurice John Humphrey, Queen Elizabeth College, Department of Chemistry, 1975 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. $M_{sub w} M_{sub n}$ **Directed Polymerization of Multiunsaturated Monomers** Thomas R. Hoffend, 1964

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