

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),

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