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Anionic polymerization of isoprene, butadiene and styrene with 3-dimethylaminopropyllithium

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The synthesis of dimethylaminopropyllithium (DMAPLi), from the corresponding chloride and lithium metal, by using high-vacuum techniques, is described. DMAPLi was purified by crystallization under vacuum. Gas chromatography–mass spectrometry analysis of the purified product, after neutralization with degassed methanol, showed the existence of ~ 2% impurities. The most important of these impurities (~ 1.5%) were tetramethylhexamethylenediamine and dimethylaminohex-1-ene. By using DMAPLi as initiator, several polymerizations of isoprene, butadiene and styrene were carried out in benzene, under high-vacuum conditions. The molecular-weight range of the polymers obtained was from about 3×10^3 to 4×10^4. The polydispersity index ($I = M_w/M_n$) of the polydienes was similar ($I < 1.1$) to those obtained with the classical initiator s-butyllithium, but the vinyl content was higher. It was found that the lower the molecular weight of the polydienes, the higher the vinyl content. In the case of styrene, the polydispersity index of the polystyrenes produced was relatively high ($I = 1.2$ to 1.5), but by adding small amounts of tetrahydrofuran or by using unpurified initiator, which contains polar impurities, the polydispersity index recovers the usual values, for molecular weights higher than $\sim 1 \times 10^4$.

(Keywords: 3-dimethylaminopropyllithium; anionic polymerization; polydispersity)

INTRODUCTION

ω-Functionalized polymers are a valuable class of materials. Owing to the ability of the functional groups to participate in a variety of physical (e.g. reversible ionic association) and chemical (e.g. chain extension, cross-linking) reactions, these materials are of both academic[1] (e.g. model networks) and commercial[2,3] (liquid rubbers) interest.

In principle any type of addition polymerization can be employed to prepare ω-functionalized polymers[4,5], but if near-monodisperse polymers are desired the choice is restricted to termination-free polymerizations[6]. This technique generates near-monodisperse living polymer chains with stable carbanionic ends, which can be easily converted into a variety of functional groups, by reaction with an appropriate electrophilic terminating agent[7].

Functional groups can also be introduced on the chain ends by using functional initiators[8]. In this case the influence of the functional group on the polydispersity and microstructure of the resulting polymers should be considered.

A way to incorporate the dimethylamino functional group at the chain end is to initiate the polymerization by 3-dimethylaminopropyllithium (DMAPLi). Eisenbach *et al.*[9] first reported the synthesis of DMAPLi and the results obtained using this initiator to polymerize α-methylstyrene, styrene and butadiene[10]. The synthesis of the initiator (in tetrahydrofuran (THF) and cyclopentane) and the polymerizations were carried out in an inert atmosphere. The initiator was used as prepared without purification. In the case of α-methylstyrene the polymers obtained had much higher number-average molecular weights than the stoichiometric ones and high polydispersity ($M_w/M_n > 1.5$). For polystyrenes and polybutadienes, not enough characterization data were given.

Worsfold[11] also prepared DMAPLi in heptane and used this initiator in order to synthesize ω-functionalized polystyrenes and polyisoprenes. The main goal of this work was to study the influence of the position of the functional group in a polymeric chain on the reactivity of the group.

Stewart *et al.*[12] have used DMAPLi prepared in hexane, after purification, to prepare low-molecular-weight polybutadienes ($M_n < 1500$) under argon. Some results on the variation of the microstructure of the polymers with respect to the amount of polar impurities in the initiator solution were given.

Fetters and coworkers[13] by using this initiator prepared amine-capped polyisoprenes, having predictable

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