APPLICATION OF Et₃NHCl-AlCl₃ IONIC LIQUID AS AN INITIATOR IN CATIONIC COPOLYMERIZATION OF 1, 3-PENTADIENE WITH STYRENE

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Abstract

Cationic copolymerization of 1,3-pentadiene (PD) with styrene (St) using the triethylamine hydrochloride-aluminium chloride (Et₃NHCl-AlCl₃) room temperature ionic liquid as an initiator in toluene has been investigated. The polymerization proceeds to high conversions, indicating high initiating reactivity of Et₃NHCl-AlCl₃ in these copolymerization systems, although molecular weights of the polymers are limited which are similar to polymerization initiated by Lewis acids such as TiCl₄, BF₃, BF₃·OEt₂. The polymers were analyzed using IR spectra in conjunction with gel permeation chromatography (GPC).

Keywords: Et₃NHCl-AlCl₃ ionic liquid, cationic copolymerization, 1,3-pentadiene, styrene

INTRODUCTION

With the development of petrochemical industry, the comprehensive utilization of C₅ fraction, a by-product from ethylene production, attracts increasingly wide...
attention. 1,3-pentadiene (PD) is the most important linear diene in the C\textsubscript{5} fraction and aliphatic petroleum resin (C\textsubscript{5} petroleum resin) is produced via PD-based cationic polymerization. Introducing another monomer copolymerized with PD, the property of petroleum resin can be improved. The cationic copolymerization of PD with another monomer initiated by various Lewis acids such as AlCl\textsubscript{3}, TiCl\textsubscript{4}, BF\textsubscript{3}, BF\textsubscript{3}-OEt\textsubscript{2}, etc., in aliphatic medium solvents has been well studied [1]. The corrosive nature and potentially environmental hazards in the case of BF\textsubscript{3}, BF\textsubscript{3}-OEt\textsubscript{2} are drawbacks of these systems.

Over the past several years, room temperature ionic liquids (RTILs) have stimulated much interest among the chemistry community for their potential as green “designer solvents and/or catalysts” and several excellent reviews are available recently [2-4]. RTILs not only show potential for use in separation processes [5] and electrochemistry [6], but also they are promising catalysts for chemical synthesis [7], due to their particular properties, such as negligible vapor pressure, wide ionic range, large electrochemical windows, etc.. In the last few years, it has been shown that ionic liquids can be advantageously used also for polymer synthesis, especially for radical polymerization [8,9] and electropolymerization [10,11]. But the application of ionic liquids in the cationic polymerization is still very limited [12,13].

The alkylation of benzene with 1-hexene [14] and synthesis of bisphenol A [15] using the Et\textsubscript{3}NHCl-AlCl\textsubscript{3} ionic liquid as catalyst have been investigated in our laboratory. In the present paper, we first report the application of Et\textsubscript{3}NHCl-AlCl\textsubscript{3} ionic liquid as an initiator in the cationic copolymerization of PD with St. The polymerization proceeds to high conversions, indicating high initiating reactivity of Et\textsubscript{3}NHCl-AlCl\textsubscript{3} in these copolymerization systems (Scheme 1).

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\begin{align*}
\text{PD} + \text{St} \quad \xrightarrow{\text{Et}_3\text{NHCl-AlCl}_3} \quad \text{PDStPDPDStStPD} \\
\text{toluene} \\
\end{align*}
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\textit{Scheme 1} Cationic copolymerization of PD with St

**EXPERIMENTAL**

**Materials**

PD and St were of analytical grade. Before use, they were dried under vacuum over calcium hydride to remove inhibitors and stored in calibrated ampoules. Toluene and methanol (Fisher, ≥ 99.8%) were used as received. Et\textsubscript{3}NHCl and AlCl\textsubscript{3} were purified by sublimation in vacuum.