Study of the Interactions of Organic Sulfides with Active Species in the Cationic Polymerization of 1,3-Pentadiene

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Summary

Different alkyl sulfides (dimethylsulfide, ditertiobutylsulfide and diphenylsulfide) were investigated in the polymerization of 1,3-pentadiene initiated by aluminum trichloride in polar solvent in order to control the polymerization and to study the interaction between the electron donor and the active species. Thus, it was found that dimethylsulfide totally inhibited the polymerization, while thanks to its steric hindrance the polymerization occurred in the presence of ditertiobutylsulfide. However, for this electron donor, a transfer activity was evidenced at room temperature and at 0°C, which contributes to prevent the control of the polymerization. Diphenylsulfide stabilizes a little the active centers with nearly no transfer reaction. However in the studied experimental conditions, the stabilization was not sufficient to obtain a living polymerization.

Introduction

In the context of our studies on the cationic polymerization of 1,3-pentadiene, part of the research was devoted to the role of various electron donors in order to control the polymerization [3]. The work was interested in the understanding of the interactions between the electron donors and the active species. Most of the time, these studies are arduous because the lifetime of the active species is limited. In the case of the system 1,3-pentadiene-AlCl₃ in non polar medium studies revealed that the active species were long-lived despite numerous side reactions such as isomerization, cyclization, polymer grafting and cross-linking [4-5]. Preliminary studies showed that in a polar medium such as in CH₂Cl₂, the polymer was soluble which gave hopes of a simpler system, i.e. with less side reactions.

In the work published by Webster, it was demonstrated that alkyl sulfides were interesting Lewis bases to achieve controlled polymerization of isobutylvinylether [1]. As the sulfide concentration was increased, the rate of polymerization decreased and a nearly monodisperse polymer was obtained. Interestingly, when the bulkiness of the sulfide was increased, the rate of polymerization increased but the system deviated
from living behavior. The present study was aiming at determining whether the same kind of observation could be collected on the 1,3-pentadiene-AlCl₃-CH₂Cl₂ system.

**Experimental part**

*Reactants*

Methylene dichloride, pentane and 1,3-pentadiene were dried under vacuum by storage over calcium hydride. Aluminum trichloride (Aldrich) was used without purification and stored in a glove box under nitrogen. The sulfides, dimethylsulfide, ditertiobutylsulfide and diphenylsulfide (Aldrich), have been dried on molecular sieves.

*Polymerizations*

The polymerizations were carried out in a three necked reactor equipped with teflon magnet, and a rubber cap. After a nitrogen flush the reactor was introduced in the glove box equipped with a balance where aluminum trichloride was stored. After introduction of the required quantity of the Lewis acid, the reactor is connected to the vacuum line and placed in a liquid nitrogen bath. The solvent and the monomer are introduced by condensation under vacuum. The liquid additive is introduced by the rubber cap with a syringe. The reactor is rapidly brought to the required temperature and allowed to stand for the required time. The polymerizations are quenched by an injection of a few mL of butylamine.

Before workup, the cross-linked polymer was separated by filtration then dried under vacuum. The filtrate was washed with water, followed by evaporation of the solvent and remaining monomer under reduced pressure. The polymer samples can be purified several times by dissolution and precipitation in order to determine the extent of incorporation of the electron donor.

**Results and discussion**

It was interesting to compare the behavior of three sulfides: dimethylsulfide (SMe₂), diphenylsulfide (SPh₂) and ditertiobutylsulfide (S(t-Bu)₂). They have been used in similar conditions to previous work so as to allow comparisons, i.e. a monomer concentration close to 1M and a Lewis acid concentration around 1.10⁻²M. In these conditions, it has been shown that at room temperature in non polar medium the initiation reaction directly takes place on the Lewis acid, without the necessity of a proton donating species [2]. Operating in polar conditions (CH₂Cl₂) the results are similar to the ones in pentane, as shown in Table 1, except the above mentioned fact that the gel content is strongly decreased.

Whatever the solvent used, the polydispersity index of the soluble polymer was very high, higher than 10. It has been shown elsewhere that this situation is due to the reaction of the polymer with growing chain ends, leading to transfer [4]. It is known that such polymer transfer, when predominant over the other transfers and the reactions interrupting chain growth, leads to a polymer with the same average number molar mass as in the absence of transfer, but of course with an increased polydispersity index. It is noteworthy that, assuming that each aluminum atom is involved in the generation of one macromolecule, the \( Mₚ \) of the three experiments carried out in CH₂Cl₂ (runs 2, 3 and 4) are close to the theoretical value (3300, 3900