NEW DEVELOPMENTS IN THE PROCESS FOR THE PRODUCTION OF POLYBUTADIENE RUBBER

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ABSTRACT

The living anionic homogeneous polymerization of 1,3 butadiene in bulk and in non-polar hydrocarbon solvents was investigated. n-Butyllithium was used as a catalyst in a very low concentration in order to obtain the highest possible percentage of cis- 1,4 polybutadiene suitable for the rubber and tire industry. It is shown that the microstructure of obtained polybutadienes is quite sensitive to the concentration of the catalyst in the polymerization medium and the presence of small amount of polar co-solvent. In bulk (without solvent), the polybutadiene obtained with 10^{-5} mol /l of n-Butyllithium contains 88% of cis-1,4 microstructure. However, a decrease in cis- 1 ,4 content is accompanied by an increase of catalyst concentration, using non-polar solvents and to a greater extent by the presence of polar co-solvent.

Nevertheless, to increase the amount of cis- 1,4 structure further, a novel experimental technique was developed. The state of the art was achieved by separating the initiation step of adding n-Butyllithium to the monomer in the reactor. 5% of the monomer were firstly po]ymerized in a preinitiation step and the resulting polybutadienyllithium was added to the main reactor containing 95% of the monomer. Thus, living anionic polymer viz., polybutadienyllithium was used as a catalyst to 1, 3-butadiene monomer.

It was concluded that by such development polybutadiene with 97% cis- 1,4 could be obtained by the anionic living polymerization process.

INTRODUCTION

1,3 butadiene, the simplest of the conjugated double bond dienes, is produced commercially by thermal cracking of petroleum fractions and by catalytic dehydrogenation of butane and butene.

High molecular weight polybutadiene homopolymers are prepared commercially by different catalytic systems, the choice of catalyst is usually governed by the desired microstructure of the product. Polymerization of butadiene can potentially lead to three poly (l,2-butadiene)s, atactic, isotactic and syndiotactic and two cis and trans forms of poly (1,4-butadiene). The percentages of microstructures vary with conditions of polymerization and all parameters of the industrial process as well as type of catalyst and reaction environment. However, high cis-1 ,4 polybutadiene rubber (BR-CIS) is one of the most important elastomers used by the rubber industry, world consumption in 1999 was estimated at almost 2.0 million metric tons, up 2.7% over the 1998 level. Future growth to year 2004 is estimated at 2.8% per year, bringing world consumption to an estimated 2.25 million metric tons [I]. Tires and tire products are responsible for 67% of consumption. Non tire applications, especially impact modification of styrenic plastics, are becoming increasingly important. The impact-modification requirement for polybutadiene rubber is 15-20% of world demand. Other non-tire uses in footwear and sport items contributing to 5-10% of BR demand.

Commercial high-cis- 1,4 polybutadienes are prepared using Ziegler-Natta polmerization catalyst derived from cobalt, nickel, neodymium and titanium. A much simpler and more economical processes based on new development of the well-known ionic living polymeriztion technique worth considering [2-4]. The process involve the use of homogenous catalytic polymerization of 1,3-butadiene in non-polar media by alkyllithium salt as a catalyst for the initiation process. The aim of this work was to increase the maximum cis- 1,4 content attainable with butyllithium initiators in a similar approach to our earlier findings [5] on the preparation of high-cis- 1,4 polyisoprene using n-butyllithium as a catalyst in non-polar solvent. Our findings with isoprene polymerization was recognized as a novel method of obtaining the highest cis-1,4-polyisoprene,analouge to natural rubber, by the anionic living polymerization technique [6].

EXPERIMENTAL

The experimental methods employed in the purification of 1,3-Butadiene polymer grade monomer and HPLC grade solvents in the present work are similar to that used in our earlier work on anionic living polymerization [7-9]. Extra care was taken to avoid the presence of water, oxygen and other impurities, which effect polymerization or react with the catalyst (initiator). n-Butyllithium (n-BuLi) of different concentrations were used similar to the way described in our early investigation [5]. A one litre polymerization glass reactor was cleaned and dried at 120 ^{0}C before use. Nitrogen of purity more than 99.999 (v/v) was dried through a series of columns of calcium hydride particles, phosphorus pentoxide, and Linde molecular sieves type 5A bubbled through living α -methylstyryl sodium tetramer before being introduced to the reactor. Prescribed amounts of the catalyst (n-BuLi) monomer (butadiene) and solvent (if used) were charged under dry nitrogen stream at 5 ^{0}C.

At the first stage 5% of the monomer were syringed into the reactor and left at 5 ^{0}C and I atm pressure for one hour.The rest of the monomer then added and left for two hours to complete the polymerization and then terminated by introducing methanol to the well-stirred reactor. Polybutadiene was purified after each run several times by dissolution-reprecipitation with the chloroform-methanol system and dried before characterization. Stereoregularity of polybutadienes obtained in this work was determined carefully from their proton and carbon-13 spectra, which were recorded on 90 MHz NMR spectrometer equipped with Fourier transfer accessory, according to the method described elsewhere [9].

RESULTS AND DISCUSSION

Our main concern in this study was to provide critical examination on the slight change of catalyst concentration in the very dilute state of n-BuLi when used in bulk (without solvent) or with n-hexane solvent during the polymerization process. The second object of the experimental findings was to further increase the cis-1 ,4-polybutadiene obtained by separating the initiation step during the polymerization process.

Results presented in Table-1 shows a remarkable increase in the cis-1,4-content when concentration of the catalyst was decreased both in n-hexane and in bulk polymerization of 1 ,3-butadiene.

Results of Table-2 demonstrate a further increase in the cis- 1.4 content when the initiation step was isolated from the propagation step.

In this work the concentration of the catalyst (n-BuLi) was kept constant at three levels of dilute concentration. Both in bulk and when using n-hexane as a polymerization solvent, the cis- 1,4 content increased with the decrease of catalyst concentration. Moreover, the presence of traces of tetrahydrofuran (THF) decreased the cis-1, 4 content further (Results presented in Table-1). Likewise, when the initiation step was separated and preiniation of 5% of the monomer acted as a catalyst for the remaining 95% of butadiene, higher cis-1, 4 content was obtained both in bulk and in non-polar media. This marked sensitivity of the stereochemistry of anionic polymerization can be traced to the structure of the propagating living polymer chain end. The presence of polar environment coming from the higher catalyst concentration or trace of polar solvent (THF),have indeed contributed to the noticed decrease in cis 1,4 structure during 1,3 butadiene polymerization.

The process described in this work can be used for the production of high (>96%) cis-1,4 polybutaidene rubber (BR-cis) to be used by tires and rubber manufacturers. These findings indicates the advantage of adopting such simple and versatile anionic living polymerization for the production of five different elastomeres viz., high cis-1,4 polybutadiene, high cis-1,4 polyisoprene, solution styrene- butadiene, styrene-butadiene-styrene, styrene-isoprene-styrene block polymers [10].

The other important factor in favour of selecting such a process is the utilization of one catalyst for the production of several commercial elastomers, using only one plant and benefiting from all available utilities. Further work on the kintic analyses , molecular weight and molecular weight distribution will be the subject of future publication.

Table (1) Microstruture of polybutadienes obtained in bulk, n-hexane and in the presence of THF (traces), using different concentration of n BuLi at 5°C.

Catalyst (n-BuLi) Mol.L	Chain microstructure (mol%) Cis-1,4	Trans 1,4	1,2	3,4
Bulk (no solvent)				
1	88	10		
5	82	14	4	
10	75	20	5	
n-hexane (solvent)				
1	80	16	4	
5	75	20	5	
10	71	22	7	
n-hexane (trace THF)				
1	44	37	19	
5	39	39	22	
10	30	35	35	

Table (2) Microstructure of polybutadiene in bulk and n-gexane using the precipitation technique at different concentration of n-BuLi and 5°C

Catalyst (n-BuLi) Mol.L	Chain microstructure (mol%) Cis-1,4	Trans 1,4	1,2	3,4
Bulk (no solvent)				
1	97	3		
5	92	7	1	
10	87	11	2	
n-hexane (solvent)				
1	85	12	3	
5	81	15	4	
10	76	17	7	

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