Purification of Styrene for Anionic Polymerization

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Synopsis

Anionic polymerization of styrene in CSTR processes demands monomers which are highly pure. Lithium aluminum hydride (LAH) is a highly reactive material which reacts with the impurities in styrene that interfere with anionic polymerization. The LAH/impurity reaction products are not compatible with anionic polymerization and therefore must be isolated or removed from the styrene before polymerization. This problem is most readily solved by supporting the LAH on ion exchange resin beads such that the impurity reaction products are chemically bound to the support. We have demonstrated the preparation of > 50 mol of polystyrene/mol of n-butyl lithium by passing the polymerization feed through a column filled with LAH/ion exchange resin. This represents > 10-fold improvement in yield (based on n-butyl lithium) over previously described feed purification techniques.

INTRODUCTION

All commercial molding and extrusion grades of polystyrene are manufactured utilizing free radical polymerization. One of the key reasons for this is the stringent feed purity needed for anionic polymerization. Thus, the key to implementation of anionic polymerization is the development of an effective and low cost feed clean-up process.

If a batch or plug-flow type process is utilized, a lower level of purity can be tolerated since the impurities are neutralized by the initiator before incipient polymerization takes place. However, for conducting polymerization in a continuous stirred tank reactor (CSTR), the feed must be highly pure since the living polymer is continuously mixed with fresh feed. The continuous termination of living anions by incoming impure feed results in low monomer conversion and the inability to produce high molecular weight polymer.

Recently, we have reported that high molecular weight polystyrene can be produced utilizing anionic polymerization in a CSTR reactor.[1] We also have reported that distillation is an especially effective way to purify anionic polymerization feed.[2-5] This allowed us to make 5 mol of polystyrene for every mole of n-butyl lithium (NBL) used due to the chain transfer to solvent inherent in the CSTR process. We now want to report a further 10-fold yield improvement by further removal of impurities that consume NBL.

APPROACH

Academic researchers in the past have purified monomers and solvents for anionic polymerization by fractional distillation and distillation from highly

reactive metallic reagents which react with water, oxygen, carbon monoxide, carbon dioxide, and organic impurities which act as terminators during anionic polymerization. The distilled monomer and solvent are used immediately or stored in a highly pure environment where they are preserved until use. In the industrial setting, it would be especially convenient to achieve the same kind of purity achieved by academic researchers, continuously as the feed enters the polymerization reactor. This concept has been demonstrated for gaseous monomers (e.g., ethylene) by sparging the crude monomer through a column filled with a highly reactive organometallic reagent (e.g., benzyl sodium) dissolved in a polyamine (e.g., N,N,N',N'-tetramethylethylene diamine).[6] Impurities such as water, oxygen, carbon monoxide, carbon dioxide, and acetylene were totally removed from the monomer at starting levels as high as 100 ppm. In another example of this same concept, gaseous monomers are passed through a "scavenging zone" containing an organometal compound such as aluminum, boron, or zinc alkyls.[7]

Since styrene is a liquid, we chose to support the reactive reagent on a heterogeneous polyamine support. The polymerization feed (as it enters the polymerizer) could then be passed through a column containing the highly reactive solid.

Supporting of metallic reagents for purification of liquids is not new. Subayya[8] treated anion exchange resin beads (containing quaternary ammonium chloride functionality) with aqueous sodium borohydride. He found the reactive beads useful for removal of aldehydes and peroxides from organic solutions and for the reduction of various metal ions.

$$\left\{-N(CH_3)_3^+ CL^- + NaBH_4 \longrightarrow \left\{-N(CH_3)_3^+ BH_4^- + NaCl\right.\right.$$

However, we found that the supported borohydride was not reactive enough to remove all of the monomer and solvent impurities affecting anionic polymerization. Thus, we chose to investigate the more reactive aluminum hydride reducing agents.

EXPERIMENTAL

Preparation of Supported Aluminum Hydride Columns

DOWEX MWA-1 macroporous weak anion exchange resin beads (available from The Dow Chemical Company) were washed with $1N$ sodium hydroxide followed by water to insure they were in the free amine form. The wet beads were dried by slurrying with ethylbenzene in a round bottom flask equipped with a Dean–Stark trap. Water was distilled from the flask until the vapor temperature reached 136°C. The ethylbenzene was decanted from the flask and the aluminum hydride solution (LAH and AlH_3 in diethyl ether; all others in toluene) added under dry nitrogen. The slurry was stirred for 1 h. The excess aluminum hydride solution was decanted from the flask. The beads were washed with fresh dry solvent to remove the excess aluminum hydride. The beads were slurried into a 316 stainless steel column (9.5 mm × 10 cm). The column was connected to a 3.175 mm Milton Roy piston pump. Dry toluene was pumped through the column until no traces of other solvents could be detected.

Evaluation of Column Performance

A toluene solution was prepared containing 1000 ppm acetophenone. The solution was pumped through the column at a rate to achieve a 2 min residence time. The effluent was collected for 10 min in a bottle open to the air. The contents of the bottle were analyzed by gas chromatography for unreacted acetophenone and the presence of α-phenethyl alcohol.

Preparation of Large Column of Ion Exchange Resin Supported Lithium Aluminum Hydride

DOWEX MWA-1 ion exchange resin beads (454 g) were placed in a 2-L round bottom flask equipped with a mechanical stirrer, a heating mantel, a nitrogen inlet tube, and a Dean–Stark trap. Ethylbenzene (500 mL) was added and water azeotropically and exhaustively distilled from the mixture (220 mL). The contents of the flask were allowed to cool to ambient temperature under dry nitrogen. The ethylbenzene was then decanted from the beads followed by the addition of 500 mL of diethyl ether saturated with lithium aluminum hydride (LAH). After stirring for 20 min, the liquid was decanted from the beads. The beads were then washed with 500 mL of dry diethyl ether. The residual solvent was evaporated from the beads by sweeping dry nitrogen through the flask. The dry beads (pyrophoric) were transfered under nitrogen to a 5 × 50 cm column. The LAH content of the beads was determined to be 8.5% by weight by taking an aliquot of the beads and measuring the volume of hydrogen (with a gas buret) released upon reaction with n-butanol.

RESULTS AND DISCUSSION

Aluminum hydrides are readily soluble in ether and amine solvents due to the attraction between the electron deficient aluminum and the electron rich heteroatoms of the solvent. Since amines have the stronger attraction for aluminum, the aluminum hydrides are readily removed from ethereal solvents by the ion exchange beads.

To study the effectiveness of the supported aluminum hydrides, acetophenone was chosen as a model impurity and toluene chosen as solvent. The acetophenone (1000 ppm) spiked toluene solution was passed through a column containing the aluminum hydrides and the effluent analyzed for acetophenone and its reduction product, α-phenethyl alcohol.

We were interested not only in the effectiveness of the supported aluminum hydride column to reduce the monomer and solvent oxidation impurities, but also in retaining the resulting aluminum alcoholates on the column. The results of the screening study are summarized in Table 1.

These results show that lithium aluminum hydride (LAH) is the only aluminum hydride tested which is both effective in completely reducing the acetophenone while retaining the reduction product (α-phenethyl alcohol) on the column. This feature is critical since both ketones and alcohols interfere with anionic polymerization.

An explanation for the exceptional performance of the LAH is that the lithium aluminum alcoholate resulting from reduction of the acetophenone

TABLE I

Aluminum hydride	Acetophenone in effluent (ppm)	α-Phenethyl alcohol detected in effluent?
BH_4^-	980	Yes
$Al(iBu)_2H$	0	Yes
$NaAl(OCH_2CH_2OCH_3)_2H_2$	130	Yes
AlH_3	0	Yes
$LiAlH_4$	0	No

still retains its affinity for the amine functional resin. With the other aluminum hydrides, the affinity of the aluminum alcoholate for the amine resin is weak enough that elution occurs. The chemistry taking place inside the supported LAH column is represented below.
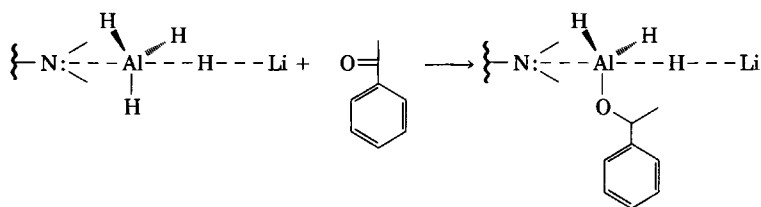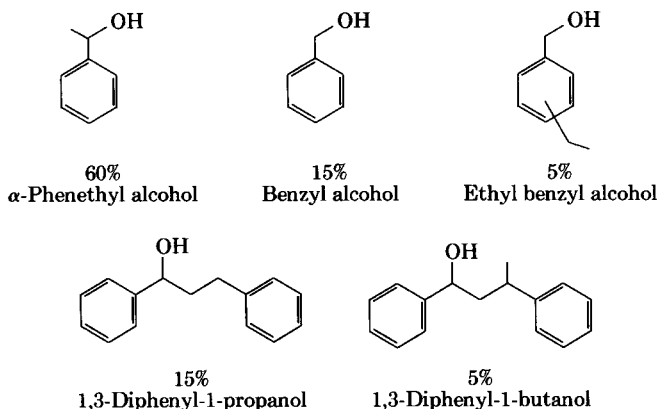

Next we chose to test the effectiveness of the resin supported LAH in actual use for anionic polymerization feed clean-up. The same polymerization apparatus and feed cleanup procedure as previously described[1] was utilized. The only change which was made was the insertion of a 5 × 50 cm column filled with supported LAH. The column was inserted in the feed line just before the feed entered the polymerization reactor. The polymerization feed consisted of 50% by weight styrene in ethylbenzene and was pumped through the column at a rate of 1 kg/h. Before insertion of the column, the reactor was operated continuously at steady state, which required 100 ppm of NBL to produce a polystyrene of 200,000 weight average molecular weight (M_w) and 98,000 number average molecular weight (M_n). After insertion of the column, only 7 ppm of NBL were required to produce polystyrene having the same molecular weight. This indicates that about 80 mol of polystyrene are produced for each mole of NBL added (615 ppm are required to make polystyrene have a number average molecular weight of 104,000 if 1 mol of polymer is made per mole of NBL). This indicates that in our previous studies, over 90% of the NBL was being consumed by impurities.

The polymerizer was operated continuously for 21 days at an NBL consumption range of 7–12 ppm at which point the NBL consumption began to increase abruptly. Gas chromatographic analysis of the column effluent showed traces of α-phenethyl and benzyl alcohols.

The column was then extracted with wet toluene and the extract analyzed by gas chromatography. Over 50 components were found. The structure and approximate relative amounts of the major (> 5% by weight) components, as determined by gas chromatography/mass spectroscopy, are shown below.

Major Impurity Reduction Products Extracted from Used LAH / Dowex Column

60%
α-Phenethyl alcohol

15%
Benzyl alcohol

5%
Ethyl benzyl alcohol

15%
1,3-Diphenyl-1-propanol

5%
1,3-Diphenyl-1-butanol

The diphenyl alcohols probably result from the condensation of acetophenone and benzaldehyde in the strongly basic and anhydrous environment inside the beads before reduction takes place.

CONCLUSIONS

The removal of final traces of water and organic impurities detrimental to anionic polymerization is readily accomplished by passing the polymerization feed stream through a column containing ion exchange resin beads which have been treated with lithium aluminum hydride. The use of this technology results in a > 10-fold improvement in polymer yield over previously described feed cleanup techniques.

References

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