Anionic Polymerization of Styrene: Integration with Styrene Monomer Production

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Synopsis

Anionic polymerization and ethylbenzene dehydrogenation were carried out in the laboratory using continuous reactor designs and conditions typical of current commercial processes. The dehydrogenator was operated at 43–55% conversion with continuous distillation of the ethylbenzene/styrene mixture to remove byproducts that would interfere with the subsequent anionic polymerization. The anionic polymerization was carried out using a reactor of the CSTR type which operated at > 99% conversion of styrene. The volatiles were recovered from the polymer syrup and recycled back to the dehydrogenator. During 4 months of continuous operation, the integrated process showed no detrimental buildup of impurities which affected the anionic polymerization or dehydrogenation. The polystyrene produced had excellent color, clarity, thermal stability, and polydispersity (M_w/M_n = 2.1–2.4). The ability to control weight average molecular weight was within a range of 20,000 using an on-line GPC in concert with a colorimeter.

INTRODUCTION

In previous studies,[1–3] it was found that anionic polymerization of styrene is industrially feasible. A process to produce broad molecular weight distribution (MWD) polystyrene (M_w/M_n = > 2.1) having excellent color utilizing a CSTR reactor design was described. Polymer quality, styrene conversion, and molecular weight control were all found to be dependent upon the ability to produce monomer feed having consistently high purity.

Because feed purity is so critical, it would be especially advantageous to integrate the anionic polymerization of styrene with the production of styrene monomer via dehydrogenation (cracking) of ethylbenzene (EB), since distillation is part of that operation. It was felt that the direct utilization of freshly distilled styrene/EB mixture would provide anionic polystyrene (APS) feedstock of the consistently high purity required to manufacture clear and colorless polystyrene.

Another advantage of integration of APS with EB cracking is that the crude styrene and EB product mixture from the cracker could be used without the need to separate the styrene from the unreacted EB. Typically, EB crackers are operated at 40–60% conversion of EB to styrene. The separation of styrene from EB requires very large capital-intensive and energy-consuming distillation columns due to their very close vapor pressures. At the onset of this work it was felt that the crude cracker effluent could be easily distilled in

a continuous manner to remove all of the impurities which interfere with anionic polymerization (water, oxygen, and oxidized organics).

The idea of monomer and polymer process integration is not new. It was investigated about 30 years ago by Arnold and co-workers.[4] Their work involved the catalytic dehydrogenation of the EB contained in the C_8 fraction from a naphtha cracker stream to form a mixture of aromatic hydrocarbons containing 15–25% styrene. The water and tars were removed from the stream via distillation. The purified mixture was treated with sodium metal in a reactor under reduced pressure at 40–75°C to anionically polymerize the styrene.

In the present study, EB of > 99% purity was used. The EB solvent stream stripped from the polymer during devolatilization was recycled back to the EB cracker. Also, n-butyllithium (NBL) was used as the anionic initiator because it is soluble in the polymerization and thus gives much higher yields of polymer based on initiator than can be achieved using heterogeneous systems such as sodium.

A reactor of the CSTR type was used for this study. It was shown in a previous study[1] that the yield of polymer based on NBL is greatly increased by using a CSTR reactor due to the higher amount of chain transfer than occurs during batch or plug flow polymerization. This high yield of polymer results in much improved polymer quality because of lower initiator residues left in the polymer.

The basic chemistry investigated during this study is shown below:
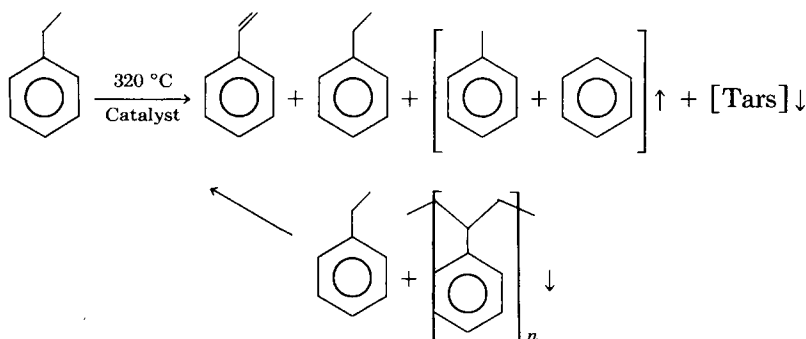
PROCESS DESCRIPTION

The following is a description of the process flow scheme and the equipment used. The material of construction throughout the process was 316 stainless steel. Figure 1 depicts the overall process.

Deionized water was pumped through a 7500-W heater using a double-headed 7 mm Milton Roy Milroyal A pump. The heater produced superheated steam at 325–340°C and 23–38 kPa (3–5 psig). An identical Milton Roy pump was used to pump EB to the top of the cracker, where it was mixed with the superheated steam and flashed adiabatically. The cracker was composed of three sections. The preheating section was approximately 122 cm long and was
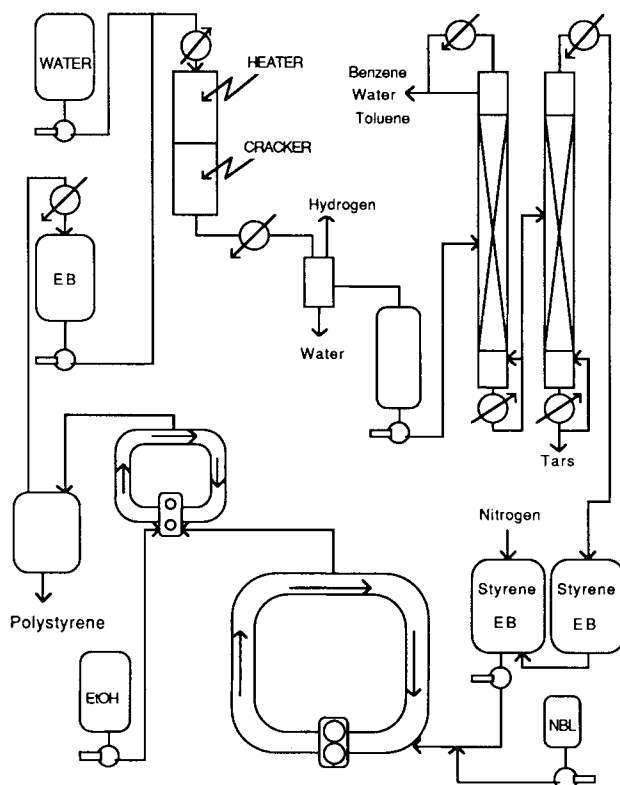
Fig. 1.   Integrated styrene production and anionic polymerization.

filled with ceramic beryl saddles to insure total vaporization of the organic phase. The 60-cm-long cracker section had a liquid hourly-space-velocity of $2.14 \ h^{-1}$. Shell 105 catalyst was used, and the cracking temperature was raised over the course of the research (4 months) from 315 to 330°C. The reactor pressure was typically 38 kPa (5 psig). The third cracker section was the cooldown section. It was approximately 60 cm in length and had a typical average temperature of 300°C. The first two sections were heated by ceramic heaters each of 2500-W capacity. A water/organic ratio of approximately 0.9 was maintained.

A water-jacketed heat exchanger immediately followed the cracker, and was used to further cool and condense the cracker effluent which subsequently entered a gas/liquid separator. This was a small, flat vessel of about 30 in.^{3} capacity which removed the hydrogen, produced during cracking, from the stream. The organic and water mixture then entered a decanter (2 L), which separated the water and crude styrene. The crude styrene receiver had a residence time of 20 h.

A third 7 mm Milton Roy Milroyal A pump was used to feed the first distillation column which had a diameter of 5 cm having 40 trays. This column was used to remove water, benzene, and toluene from the crude

styrene/EB mixture. The column pressure was maintained at 130 mm Hg, and the bottoms temperature at 90°C. The reboiler was a water-jacketed coil, which was recirculated by a Gould centrifugal pump fitted with a double-mechanical seal. The reflux ratio was 5:1.

The second distillation column was a 10 cm diameter packed column with 40 trays. This column was used to remove tars and was run at 110 mm Hg with a bottoms temperature of 85°C. A polymerization inhibitor and 4-isopropyltoluene were added to the column reboiler as a flux oil. This mixture was replenished every 4 days. The reflux ratio was 10:1. The reboiler configuration was identical to that of the first column, and both columns were packed with stainless steel 0.5 cm protruded saddles. In addition, both columns were fitted with water-cooled condensers and had residence times of about 2 h.

The overheads from the second column were collected in a tank which was transferred daily into a second tank which served as the polymerizer feed tank. Both of these tanks had a residence time of 24 h and were blanketed with highly purified nitrogen (< 1 ppm each of oxygen and water). A double-headed 1/4 in. Milton Roy Milroyal A pump was used to feed the styrene/EB mixture to the polymerization reactor.

The polymerization reactor and polymer syrup devolatilizer were the same as previously described.[1] Polymerization temperature was held at 95°C. The volatile components from the polymer syrup were condensed in a refrigerated coil heat exchanger and eventually were recycled to the cracker EB feed tank. Molecular weight measurement in the reactor was accomplished using on-line colorimetry/size exclusion chromatography as described previously.[2,3]

DISCUSSION OF RESEARCH

The primary objectives of this research were twofold. The first was to see if integration of styrene monomer production and anionic polymerization would be an economic solution to obtaining highly "anionically pure" styrene feedstock. The second objective was to determine if continuous integration, over long periods of time, would result in the buildup of impurities which would be detrimental to the cracker catalyst life, the anionic polymerization or the quality of the polymer.

To accomplish these objectives, the levels of major (> 1%) constituents (benzene, toluene, styrene, and EB) were monitored daily using gas chromatography. Regular checks were also made on minor impurity levels using capillary gas chromatography. The minor impurities monitored include: propylbenzenes, phenylacetylene, α-methylstyrene, benzaldehyde, and acetophenone. These compounds were selected to study because of their initially relatively high concentrations and their boiling points which reduced their exit path possibilities, thus making them candidates for potential buildup to detrimental levels. The buildup of any of these compounds was a concern since it would indicate the lack of a sufficient pathway out of the process for that particular compound. The discussion that follows will examine these concerns from a unit operations viewpoint centering around the cracking, distillation, and polymerization operations.
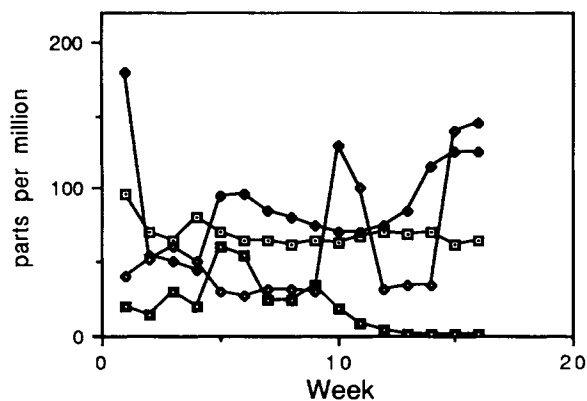
Fig. 2. Impurities in polymerizer feed: (□) phenylacetylene; (◆) propylbenzenes; (■) benzaldehyde; (◆) α-methylstyrene.

CRACKING RESULTS

Longevity of the cracking catalyst, conversion, and yield were of key interest. A dramatic loss of conversion, indicating catalyst poisoning, is always a critical concern when doing this type of study. During the 4 months of continuous operation in this study, no evidence of catalyst poisoning was observed. The styrene content of cracker effluent during the 4 months of operation ranged from 40 to 57% styrene.

DISTILLATION

As mentioned previously, one of the major benefits of integrating cracking with anionic polymerization is the elimination of the need to fractionate styrene from EB. The only purification required is the removal of the impurities which interfere with the polymerization (e.g., water, oxygen, aldehydes, ketones, and epoxides). To accomplish the purification in a continuous manner, two distillation columns were used.

The distillation columns were found to provide a very pure feedstock for the anionic polymerization when free of air leaks. At the beginning of this study, the feed contained high levels of styrene oxidation products. Since the feed to the distillation columns was free of these compounds, it was obvious that oxidation was taking place in the columns. Efforts to tighten connections and seal all potential leak points led to a continual reduction of benzaldehyde in the polymerization feed during this study. Figure 2 shows the minor impurities while Figure 3 shows the styrene concentration in the polymerization feed during this study.

POLYMERIZATION

During the course of this study, polystyrene was produced with weight average molecular weight (M_w) ranges (i.e., 200,000–310,000 M_w) and polydispersities (M_w/M_n = 2.1–2.4) typical of molding and extrusion grades. This
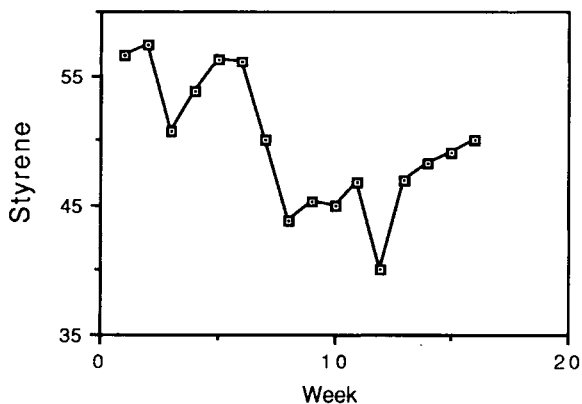
Fig. 3.   Styrene concentration in polymerizer feed.

was done to insure that the entire range of products could be made and that no significant alteration of polymerization kinetics had occurred due to integration, which would prohibit the manufacture of the higher M_w products due to impurities which cause premature termination or chain transfer. In addition, it was felt important to see if the steady state level of the impurities had any negative affect on the polymer color and clarity or on the ability to control the polymer M_w. Thus the primary areas of study with regard to the polymerizer performance were polymer color, clarity, conversion of styrene, initiator consumption, and M_w control.

After running the integrated process continuously for 2 months, the ability of the molecular weight control scheme[2,3] to maintain an acceptable M_w range was tested. Figure 4 shows the results of 4 days of continuous operation, with the M_w recorded at 5-h increments. The product aim M_w was 300,000. The control range (20,000 M_w) is typical for current polystyrene production specifications.
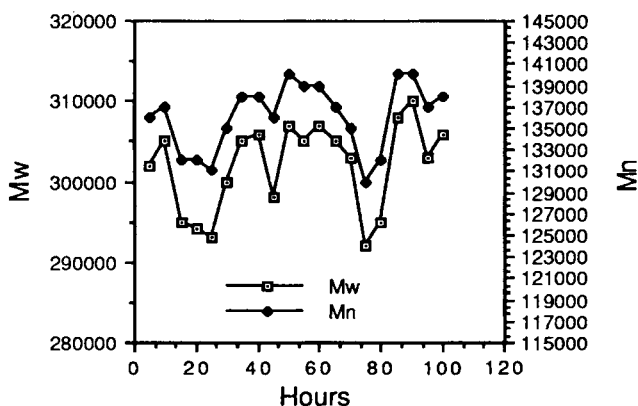

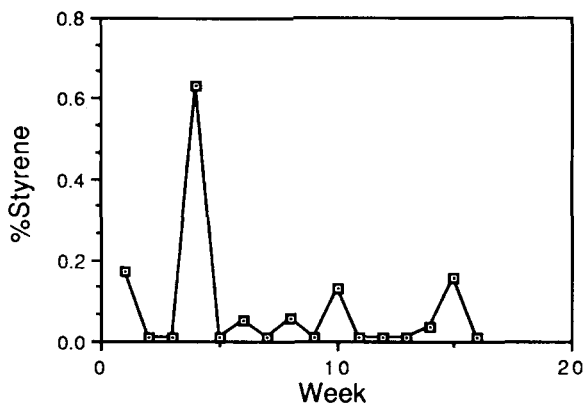Fig. 4.   Molecular weight control over 4 days: ($\square$) M_w; ($\blacklozenge$) M_n.
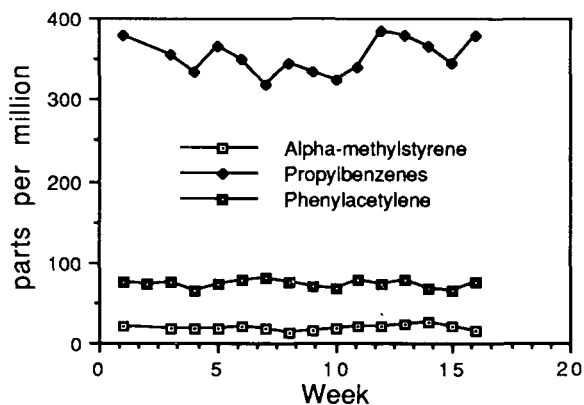
Fig. 5. Percent styrene in devolatilizer effluent.

Fig. 6. Impurities in devolatilizer effluent: (□) α-methylstyrene; (◆) propylbenzenes; (■) phenylacetylene.

The conversion of styrene to polystyrene during the polymerization was > 99%. Thus the effluent from the devolatilizer was > 99% EB (Fig. 5 shows the styrene concentration in the devolatilizer effluent during the course of this study). Maintaining this high conversion is important so that excessive styrene is not recycled back to the cracker which would result in decreased yield.

Figure 6 shows the components other than ethylbenzene and styrene in the devolatilizer effluent being recycled back to the cracker.

POLYMER QUALITY

The color and clarity of the polystyrene produced was poor during the early stages of this study due to high NBL usage. However, as the air leaks in the distillation columns were sealed, the level of styrene oxidation products (e.g., benzaldehyde) were virtually eliminated (see Fig. 2) which decreased the NBL
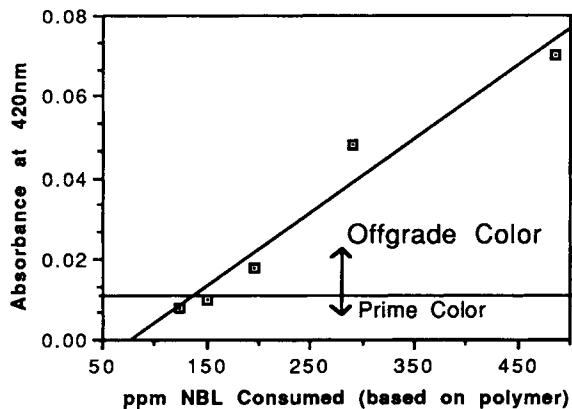
Fig. 7.   Polymer color vs. NBL usage.

consumption. Once the NBL consumption was reduced below 150 ppm (based on polymer), the color and clarity of the polymer was excellent (Fig. 7).[1]

Styrene monomer has an extremely low taste and odor threshold which is a problem in food packaging applications. To achieve low residual styrene in conventional polystyrene, special processing steps are needed.[5] One of the key advantages of APS over conventional polystyrene is the low amount of styrene monomer in the polymer due to the high monomer conversion achieved during the polymerization. This advantage is lost, however, if the APS made using this process has poor thermal stability such that styrene monomer is generated at a fast rate upon thermal processing. "Weak links" are known to play an important role in the initiation of the thermal degradation of poly-styrene.[6]

To compare the relative thermal processing stability of APS relative to conventional polystyrene, the M_w loss and styrene monomer levels were measured before and after heating. Since thermal processing of plastics is
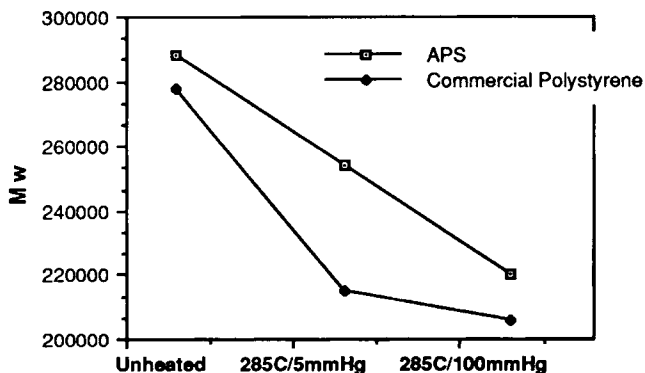

Fig. 8. M_w degradation upon heating: (□) APS; (◆) commercial polystyrene.
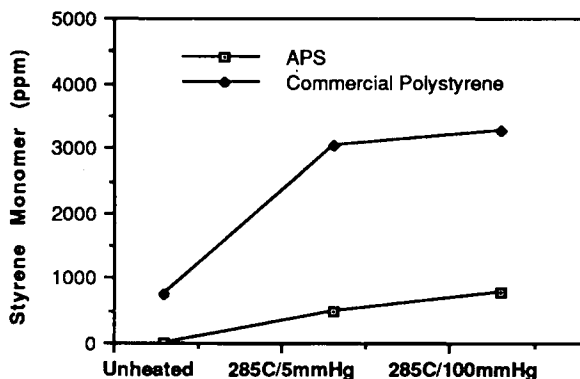
Fig. 9. Styrene generation upon heating: (□) APS; (◆) commercial polystyrene.

usually not performed in the strict absence of air, the affect of oxygen was also determined by heating the polymers at 285°C for 2.5 h in glass ampoules sealed under high (5 mm Hg), as well as, low (100 mm Hg) vacuum.

The results of these experiments (Figs. 8 and 9) show that the APS made using this process is more thermally stable than commercial polystyrenes manufactured using free radical processes from the aspect of both M_w loss and styrene monomer generation.

ANALYSES

The levels of impurities were monitored using capillary gas chromatography. A 50-m carbowax 20M column was used with a temperature program of 70°C for 16 min followed by a linear ramp to 150°C at 8°C/min. The internal standard (o-dichlorobenzene) method was used.

The level of residual styrene in the polymers was measured using gas chromatography. A 7 mm ID glass column 6 ft long packed with 3% SP2100 on 100/120 Supelcoport was used. The residual styrene was extracted form the polymer by dissolving the polymer in propylene oxide containing t-butylbenzene as internal standard. The polymer was precipitated from this solution by the addition of an equal volume of water.

Polystyrene molecular weights were determined using size exclusion chromatography. Dupont Zorbax trimodal mixed bed columns were used.

CONCLUSIONS

This study shows that integration of styrene monomer production with the anionic polymerization of styrene is an excellent concept. The feed to the anionic polymerizer produced via continuous distillation of the cracker effluent is of high purity so that high quality polystyrene can be produced with precise molecular weight control. No buildup of impurities which are detrimental to the anionic polymerization, polymer quality, or the cracking cata-

lyst was found during 4 months of continuous operation indicating sufficient impurity exit pathways from the process exist.

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