

Anionic Polymerization of Styrene: The Search for an Industrial Process

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Synopsis

Anionic polymerizations were carried out in the laboratory using a CSTR reactor design and conditions typical of current commercial mass polystyrene plants. Polystyrene having excellent color and polydispersity was produced. Polymer quality, styrene conversion, and molecular weight control were all linked to use of polymerization feed of consistently high purity and polymerization in the 90–110°C temperature range. The results of this study clearly show that high quality polystyrene can be made utilizing anionic polymerization chemistry in existing well mixed mass polystyrene reactors of the CSTR design. The key to the successful practice of this technology is the ability to produce consistently high purity polymerization feed.

INTRODUCTION

The anionic polymerization of styrene (APS) has been known for over 70 years,¹ and has been the subject of numerous academic investigations.^{2–12} Nonetheless, all commercial, molding and extrusion grades of polystyrene are produced using free radical chemistry. To justify implementation of anionic technology for polystyrene, one must demonstrate significant process and/or product advantages over free radical chemistry. Therefore, a primary objective of this effort was to identify potential process and/or product advantages that this chemistry might offer, and to determine the key areas of technology that would need further development in order to successfully commercialize an anionic process.

Review of the literature shows that anionic polymerization chemistry is well understood for batch polymerization using *n*-butyllithium (NBL) initiation. The necessity for purification of the monomer and solvent prior to polymerization has been clearly demonstrated. Furthermore, studies with plug-flow reactors have shown a strong tendency toward reactor plugging due to an accelerating buildup of high molecular weight polymer on the reactor walls.¹³ In all of these systems, molecular weight control has been difficult,¹⁴ and the reactor kinetics have led to narrow polydispersities [weight average molecular weight (M_w)/number average molecular weight (M_n) < 1.5]. Typically, the resultant polymer color and clarity are of lower quality than comparable free-radical polymers. By comparison, anionic chemistry in continuous backmixed reactors has been shown to be very complex and is not well understood.¹⁵

Several possible process and product advantages of anionic over free-radical polymerization capitalize on the differences in polymerization kinetics. Very

high monomer conversion is typical of anionic polymerizations, and the chain transfer to solvent in an anionic system is lowered, allowing production of high molecular weight ($M_w > 275,000$) polymer in dilute solution. Commercial free-radical, continuous reactions require that reactor feedstocks contain $> 80\%$ styrene in most situations, whereas an anionic feedstock would contain monomer levels equal to the final desired polymer content. This can be advantageous in a commercial setting in terms of conversion cost, and the low steady-state reactor monomer levels minimize runaway potential. Further, high molecular weight polymer can be produced at very high polymerization rates, while free-radical polymerizations suffer a 50% rate decrease in producing polystyrene with $M_w = 300,000$ vs. 200,000. Finally, APS is essentially free of styrene dimer and trimer which are inherent in free-radical polystyrene (FRPS). These contaminants have a plasticizing effect resulting in a decrease in glass transition temperature and lead to other processing problems such as die drip and mold sweat.

One potential commercially attractive feature of an anionic process relates to the fact that the major route for manufacture of styrene is via dehydrogenation of ethylbenzene. Typically ethylbenzene crackers operate at low conversion (40–50%) of ethylbenzene in order to maintain high yields. The styrene is isolated from the cracker effluent by distillation using capital-intensive columns at high reflux ratios, necessary due to the low relative volatility difference between ethylbenzene and styrene. The implication of the lower chain transfer from solvent in APS is that the potential exists for direct polymerization of ethylbenzene cracker effluent without isolation of styrene.¹⁶ Elimination of this separation step could result in a raw material cost advantage over FRPS. Once the styrene is polymerized, the ethylbenzene could be recycled back to the cracker. Also, the high monomer conversion achieved in APS should lead to a polymer having very low residual styrene. To achieve low residual styrene in FRPS, special finishing operations are required^{17,18} which significantly add to the manufacturing costs.

It was felt that the key technological developments needed for APS to be commercially successful were:

1. Economical purification of the reactor feed.
2. Precise molecular weight control.
3. Production of polymer having a molecular weight polydispersity (MWD) of > 2 for favorable molding rheology.
4. Production of polymer meeting current FRPS color and clarity specifications.

APPROACH

Before the onset of the experimental work, it was decided to investigate only continuous stirred tank reactors (CSTR). This reactor design should inherently produce polymer with a polydispersity much broader than that achieved using plug flow processes,¹⁵ and should give a high degree of mixing which would minimize the potential of reactor plugging. Also, rates can be easily controlled by operating in a monomer-starved condition. Up to now, commercial interest has substantially focused on the value of the high poly-

merization rates of anionic chemistry, envisioning a solvent-free bulk continuous polymerization. This process, however, would require significant technical issues to be resolved. Among these would be heat transfer, viscosity constraints, terminator mixing, and molecular weight control, all possibly requiring novel reactor designs. Further, it was felt that development of an anionic process adaptable to an existing commercial capital base would offer the best opportunity.

Normal butyllithium (NBL) was chosen as the initiator because significant knowledge exists about its use and safe handling in commercial-scale operations and it provides a homogeneous initiator system, as opposed to heterogeneous systems such as sodium alkyls.

Ethylbenzene (EB) was chosen as the solvent since it is commonly used in polystyrene solution polymerizations and also would be required if a coupled styrene monomer/anionic polystyrene process, as described above, was desired.

EXPERIMENTAL

Feed Control System

High purity (> 99.8%) styrene (stabilized with 3 ppm 4-*t*-butylcatechol) and EB that had been freshly produced by The Dow Chemical Co. were used for this study. They were further purified by pumping them through Union Carbide Linde 3A molecular sieves prior to polymerization. NBL was purchased from the Foote Mineral Co. as a 15% solution in heptane in cylinders. This solution was diluted to 1.5 wt % active NBL in heptane and placed in a graduated tank. The styrene, EB, and NBL solutions were pumped into the reactor using 7-mm. Milton Roy Milroyal A piston metering pumps.

In this continuous process, the M_w of the polymer was controlled by maintaining a constant [living polystyryl anion]:[monomer] ratio in the reactor at steady state. To accomplish this, the absorbance of the reactor effluent was continuously measured using a Brinkmann Model PC/1000 colorimeter. Then, the rate of the NBL pump was controlled to maintain a constant absorbance (at 450 nm) of the reactor effluent. To compensate for measurement inaccuracies caused by instrument drift, probe fouling, etc., the absorbance control setpoint was periodically adjusted by input from either an on-line or laboratory size exclusion chromatograph M_w determination, in effect creating a master/slave control system. This control technique would at the same time compensate for the effects of absorbance in this wavelength of other contaminant species. This control system is described in more detail elsewhere.¹⁹

Reactor Design and Operation

The CSTR design chosen for this initial investigation was a recirculated coil²⁰ as depicted in Figure 1. The recirculation pump was a Northern gear pump Model 4448 which was operated at 200 rpm. The styrene, ethylbenzene, and NBL were pumped directly into the suction side of the recirculation pump to allow initial mixing. Pressure inside the coil was regulated at 383 kPa

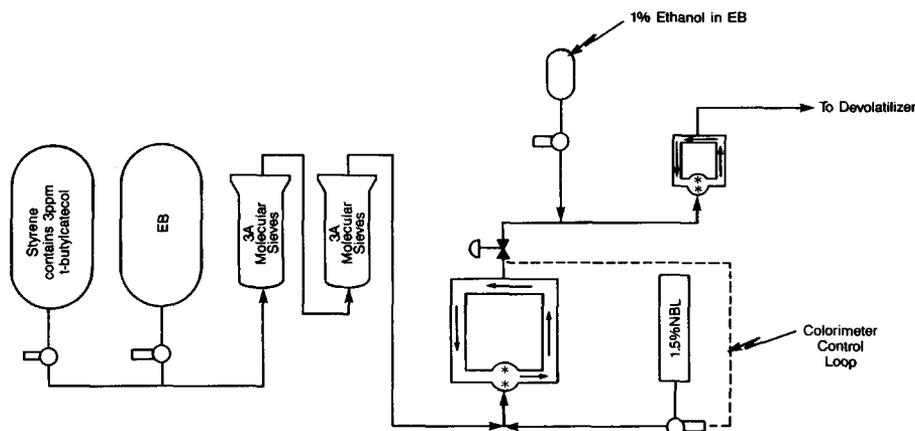


Fig. 1. Diagram of basis process.

(50 psig) using a control valve in the reactor discharge line. The coil was constructed of 25-mm ID 316 SS tubing connected in a square configuration. The tubing was jacketed and heated with water. Thermocouple ports were located at the corners of the coil. The reactor had a total volume of 1.87 L. Throughout this work the degree of backmixing (reactor recirculation rate/feed rate) was held constant at 100:1.

The reactor conditions for the experimental runs were chosen considering future scale-up to existing FRPS production scale plants. Using the design capacity of the finishing equipment (devolatilization and pelletizing), the product rate can be set. From known viscosity limitations of the reactor and devolatilizing unit operations, the feed composition (at 100% conversion of monomer to polymer) can be selected. Lastly, at a set reactor volume, the reactor residence time is then fixed.

Given the above rationale, primary to the selection of the reactor conditions is an understanding of the overall viscosity constraints. Typical CSTR-type commercial polystyrene reactors are designed to operate in the range of 200–300 P (zero shear) as a maximum viscosity. Also, both conversion cost considerations and finishing limitations require that the polymer content of the reactor effluent be maintained near that of current free-radical CSTR processes (40–70% polymer). These limitations clearly require that a viable commercial anionic polymerization system operates at a temperature much higher than commonly studied in most academic work (0–50°C). With the above in mind, the temperature range selected for study was 80–140°C, which corresponds to a viscosity range of 50–315 P, at a polymer concentration of 50 wt % and an M_w of 250,000. The styrene to ethylbenzene weight ratio in the feed was 1:1, and the reactor residence time was set at 2 h.

For initial startup of the CSTR, styrene, ethylbenzene, and NBL were all pumped into the empty reactor. The NBL was introduced at a high concentration to insure the styrene was being converted to low molecular weight polymer during filling. Once the reactor was full, the NBL pump was stopped while still pumping feed. As the color began to fade, the NBL pump was placed on colorimeter control to maintain a specified absorbance. After startup or after the changing of a variable, samples were not collected for at least

6 h (three residence times) to insure that steady state conditions had been achieved.

Terminator Mixer Design

The design of the terminator mixer was identical to the polymerization coil except it was downsized to 0.47 L. The terminator solution (1 wt % alcohol in ethylbenzene) was pumped into the transfer line between the two coils at a rate to insure complete termination of polystyryllithium prior to devolatilization.

Devolatilizer System

The polymer syrup from the terminator coil was passed into a 25-mm devolatilizing extruder operated at 240°C and 5–10 mm Hg.

Analysis

The key data desired from these initial experiments were styrene conversion, MWD, polymer color, and NBL consumption. Styrene conversion was determined by collecting a sample of the polymer syrup from the polymerizer and quenching it by shaking with a 1% acetic acid in heptane solution for at least 30 min. Since polystyrene is not soluble in heptane, the EB and unreacted styrene were extracted from the polymer during the shaking operation. Gas chromatographic analysis of the heptane extract gave the styrene:EB ratio from which % styrene conversion could be easily calculated since the styrene:EB ratio in the feed to the polymerizer was 1:1 by weight. Molecular weight analyses were performed using size exclusion chromatography calibrated against a broad polydispersity (2.5) polystyrene standard. The yellowness index of the polymer (1/8-in.-thick disc) was measured at 420 nm using a Varian Model 635 spectrophotometer with a reflectance attachment. The concentration of the NBL solution being pumped to the polymerization reactor was determined using the double titration method of Gilman and Haubein.²¹

RESULTS

Chain transfer to solvent²² (CTS) was found to be a key factor during this study. Most of the prior APS studies used benzene as solvent primarily to eliminate CTS. Also, batch polymerization inherently gives much lower CTS than CSTR processes due to the large difference in monomer:solvent concentration ratios. In anionic batch or plug-flow polymerization, the living polymer sees a high monomer:solvent ratio until the end of the polymerization. However, in the CSTR process the steady-state conversion of monomer is typically > 98%, thus giving a very low monomer:solvent ratio (< 1:25). Since the polystyryllithium is always in an extremely solvent rich environment, CTS is very high.

In batch or plug-flow anionic processes the termination of living polymer by impurities is virtually eliminated since the impurities react much faster with NBL than styrene. Thus, incipient polymerization does not occur until all the impurities have been blanked. However, in the CSTR case, the impurities are continually being added in the feed and represent a primary source of

TABLE I
Effect of Temperature on the Anionic Polymerization of Styrene

Temp (°C)	Styrene conversion (%)	M_w	M_n	NBL (ppm) ^a	Yellowness index
80	99.2	146,000	70,000	560	—
90	99.0	248,000	111,000	124	0.008
92	98.2	211,000	97,000	134	—
92	98.0	206,000	92,000	170	0.012
92	96.8	234,000	107,000	370	—
92	95.0	215,000	102,000	510	—
93	96.6	207,000	96,000	486	0.070
94	98.0	211,000	95,000	332	—
95	98.4	203,000	92,000	196	0.018
96	96.8	298,000	134,000	290	0.048
109	91.6	238,000	114,000	710	—
110	98.8	258,000	110,000	254	0.032
120	99.0	174,000	76,000	352	—
130	99.2	128,000	52,000	344	—
140	—	242,000	100,000	260	—

^aPart per million by weight NBL in solid polymer

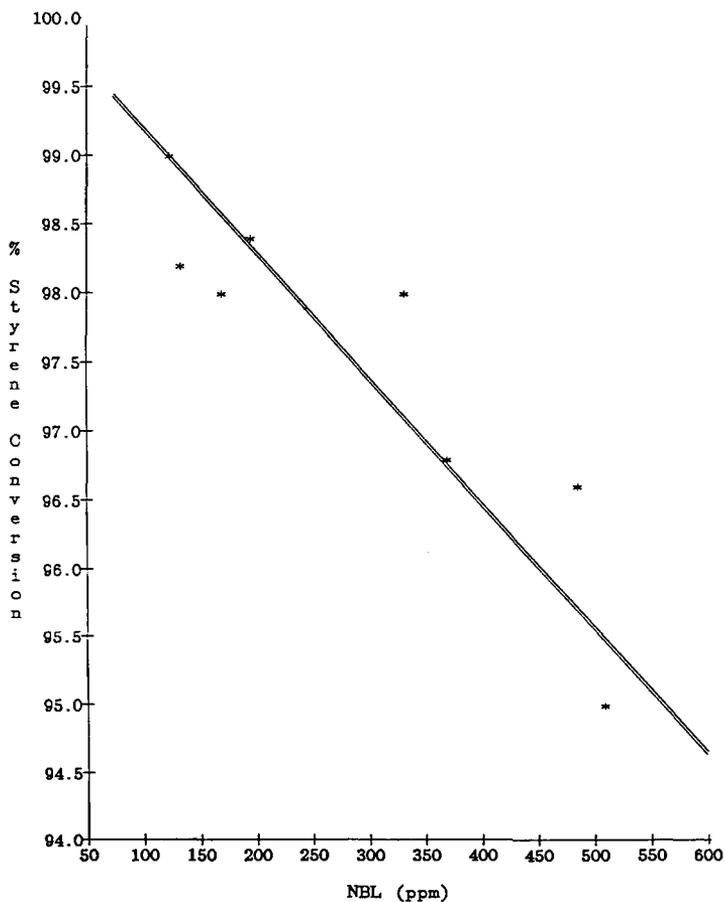


Fig. 2. Styrene conversion vs. NBL at 90–96°C.

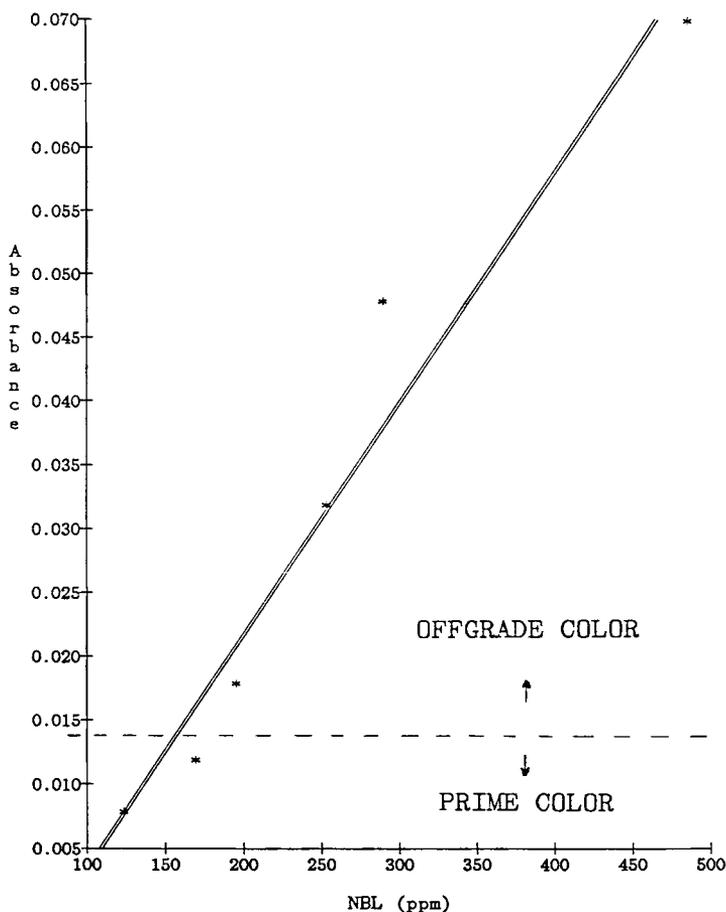


Fig. 3. Yellowness vs. NBL.

termination. Another source of termination in this study is the elimination of lithium hydride due to the relatively high temperature range studied.²³

Termination in one sense is unfavorable because it decreases the steady-state concentration of active chain ends which are needed to achieve high monomer conversion. However, termination by CTS is very beneficial because it increases the efficiency of the initiator. This increased efficiency not only leads to improved economics, but, as shown in Figure 3, was found to be essential to achieve good polymer color. Figure 3 also shows that it would be impossible to obtain prime color molding grade APS without CTS because 500 ppm of NBL would be required to produce polymer in the 75,000–125,000 M_n range. This work has demonstrated the production of APS having an M_n of 111,000 using only 124 ppm NBL (Table I). This represents almost a 500% yield of polymer based on NBL or five polystyrene chains made for every molecule of NBL used.

The importance of feed purity is shown in both Figures 2 and 3. As the feed purity decreases, not only is more NBL consumed, resulting in increased polymer yellowness, but also a decrease occurs in the conversion of styrene

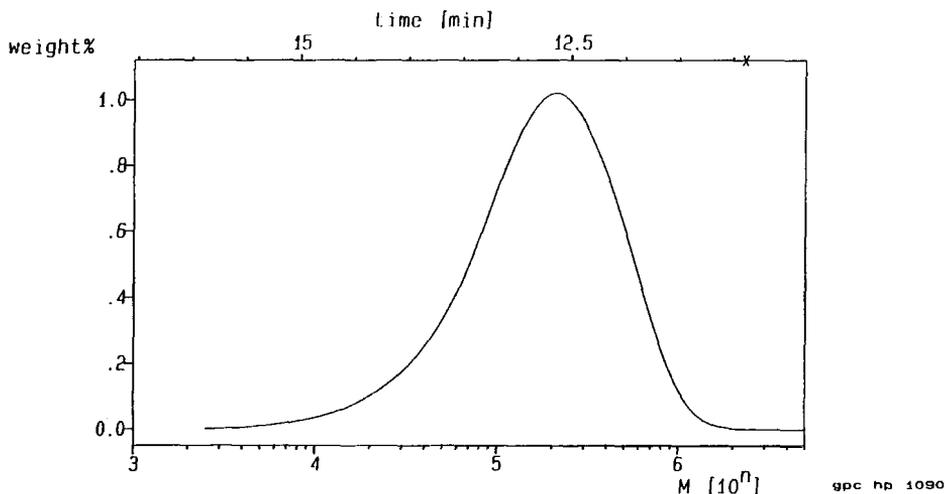


Fig. 4. GPC response curve of typical anionic polystyrene made at temperatures $< 110^{\circ}\text{C}$.

due to excessive termination by impurities. Also, it was seen that when the NBL consumption was high, the molecular weight control was more difficult due to a decrease in the steady-state concentration of the polystyryllithium, and a resultant increase in sensitivity to changes in impurity levels.

Another factor which led to poor molecular weight control was high temperature, i.e., at polymerization temperatures $> 110^{\circ}\text{C}$, a small change in the addition rate of NBL caused a large change in PS molecular weight. Again, this is due to a decrease in the steady-state concentration of active polystyryllithium chain ends, caused in this case by elimination of lithium hydride. Thus, molecular weight control and polymer quality are critically dependent upon feed purity and polymerization temperature.

The molecular weight control scheme discussed above was critical to the control of this continuous process. Any sudden changes in feed purity were

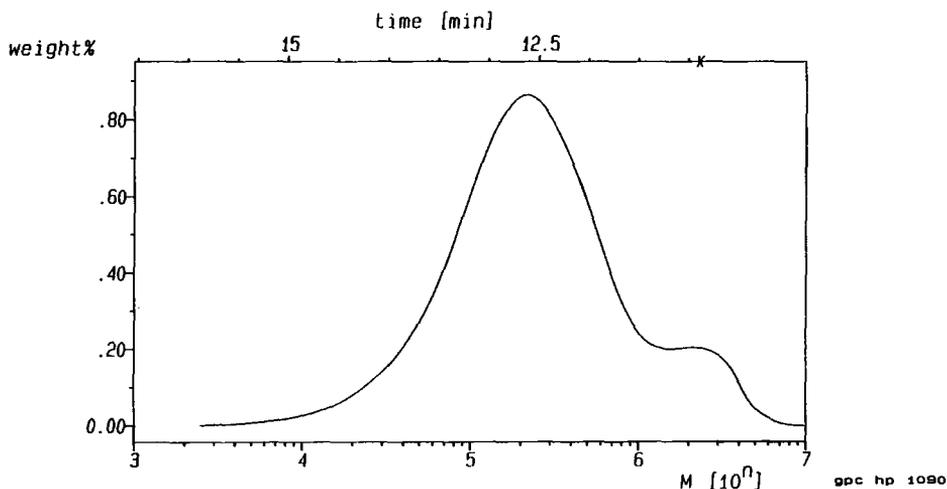


Fig. 5. GPC response curve of an anionic polystyrene made at 120°C .

immediately sensed by a change in absorbance which quickly caused the NBL pump to respond. Since some organic impurities once neutralized by NBL, have an absorbance at 450 nm, a periodic (2 h) adjustment of the absorbance setpoint was automatically made by the on-line SEC. As long as the feed was of high purity and the polymerization temperature was $< 110^{\circ}\text{C}$, this control scheme maintained the number-average molecular weight to within 5000 of the setpoint over several days of continuous operation.

When operating in the $80\text{--}110^{\circ}\text{C}$ temperature range, the MWD always fell in the 2.1–2.4 range (Fig. 4). However, at temperatures $> 110^{\circ}\text{C}$, not only was molecular weight control difficult, but the MWD curve showed the formation of a high molecular weight fraction (Fig. 5). The high molecular weight fraction was decreased by increasing the recirculation (mixing) of the reactor. At the high temperatures the rate of change of molecular weight vs. concentration of NBL is so great that mixing becomes extremely important to maintain a homogeneous NBL/styrene monomer ratio throughout the reactor. Any inhomogeneity in this balance will result in different molecular weight polystyrene being produced in the different regions of the reactor. This phenomenon is well described in the discussion of micromixing by Levenspiel.²⁴

CONCLUSIONS

From the industrial perspective, anionic polymerization of styrene has significant potential. This work has shown that broad MWD ($M_w/M_n = 2.1\text{--}2.4$) polymer having good color can be produced via anionic chemistry utilizing a CSTR reactor design and conditions typical of current commercial mass polystyrene plants. Polymer quality, styrene conversion, and molecular weight control are all linked to production of feed having consistent high purity. The use of molecular sieves alone is not sufficient to maintain a consistent high purity.

Because feed purity is so critical, it would be especially advantageous to integrate APS with an EB cracking operation since distillation is part of that operation. The direct utilization of freshly distilled styrene/EB mixture would likely provide APS feedstock of the consistently high purity necessary to manufacture prime polystyrene.

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