Catalytic Reduction of Residual Styrene Monomer in Polystyrene

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ABSTRACT: Styrene monomer has a low taste and odor threshold, and its presence in the polystyrene used in food packaging applications must be as low as possible. Conventional devolatilization technology does not lower styrene contents to desired levels, so special costly devolatilization techniques have to be used. Attempts to employ scavengers for styrene to reduce residual monomer levels have been largely unsuccessful. This article evaluates the possibility that strong acids can be used to induce residual styrene to alkylate styrene units in polystyrene by Friedel–Crafts reactions. The results of studies evaluating this approach indicate its feasibility, but colored products are obtained when sulfonic acids are used and prohibitively high levels of acids must be used to be effective. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1786–1791, 2002

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INTRODUCTION

Over 20 billion pounds of polystyrene (PS) resins are produced each year worldwide. The low cost, clarity, high glass-transition temperature, and ease of fabrication of PS make it the preferred resin for food packaging and disposable serviceware. Most of the PS produced globally is made using free-radical bulk polymerization processes. These processes (Fig. 1) polymerize styrene to only about 75% conversion. Unreacted styrene is removed by heating under a vacuum at high temperature. The level of residual styrene monomer left in the resin is typically in the 300–1000 ppm range. Because styrene has a relatively low threshold for taste and odor, its desirable level in the PS used for food packaging is <300 ppm.

There have been many prior efforts to develop technology to decrease the level of residual monomer in PS. These include the use of specialized equipment and devices, such as steam stripping,[1] centrifugal devolatilization,[2] and ultrasonic bubble nucleation.[3] Such approaches to this problem, which are primarily engineering, are limited by equilibration of the monomer with the polymer at elevated temperatures.[4] This places a lower limit on the attainable residual styrene levels, as is indicated by the data in Figure 2. Treatment of the final polymer using electron beam or ionizing radiation[5] and the use of scavengers such as unsaturated fatty acids and aldehydes,[6] sulfonyl hydrazides,[7] cyclopentadienes,[8] benzocyclobutenes,[9] styrene-*b*-butadiene resin,[10] and terpenes[11] have been considered as means to further reduce styrene levels. There is an inherent difficulty in the
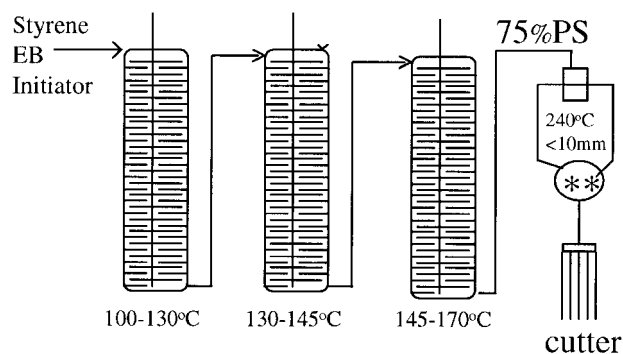
Figure 1 The most widely utilized polystyrene process; EB, ethylbenzene.

Scheme 1 The alkylation of polystyrene by the styrene monomer.

use of scavengers for this purpose, which is that small molecules in very low concentration must diffuse together and react in a viscous polymer matrix. The obvious way to overcome this difficulty would be to use the scavenger in a higher than stoichiometric concentration, but this would introduce contamination of the polymer with a new material and result in increased raw material costs. The purpose of the present article is to evaluate the possibility that PS *itself* might be used as a scavenger for residual styrene monomer in PS. It occurred to us that residual styrene could be induced to alkylate phenyl rings in PS by Friedel–Crafts reactions, as depicted in Scheme 1.

This approach has the advantage over a conventional scavenger approach that PS units are present in a huge stoichiometric excess relative to residual styrene. It was therefore hoped that only
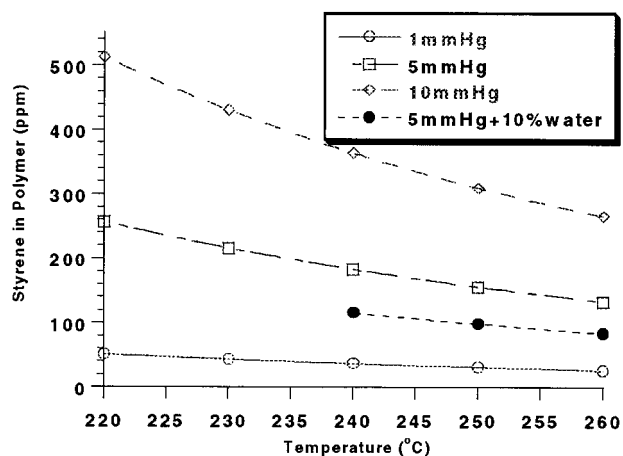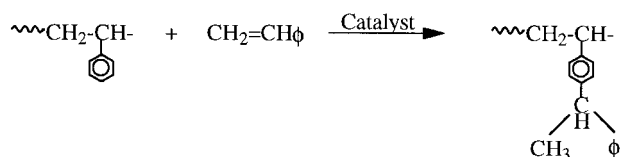
a trace amount of catalyst would be required for the process.

RESULTS AND DISCUSSION

The question of how and when to introduce the catalyst to the polymerization mixture arose in evaluating this approach. The simplest method would be to put the catalyst in the styrene monomer being fed to a continuous bulk polymerization system. Then the polymer would be produced with the catalyst molecularly dispersed in it. We investigated this approach first by employing static bulk polymerization experiments and later studied latent acid catalysts (i.e., thermally labile esters that form acids at high temperatures).

Polymerizations and subsequent heat treatments were conducted in glass ampoules. The ampoules were charged with styrene containing either 1000 or 1400 ppm of di-*t*-butyl peroxide (DtBP). The ampoules were sealed using the freeze–thaw technique to remove dissolved gases and placed in an oven at 135°C for 6 h. The polymerization mixtures were subsequently heated further at either 240 or 260°C for various times to simulate high temperature devolatilization. Control polymerizations of styrene with DtBP as the initiator were also conducted. The levels of residual styrene monomer in the polymer and the polymer molecular weight and polydispersity were determined using head-space gas chromatography (6% relative standard deviation, 10-ppm detection limit) and gel-permeation chromatography (2% relative standard deviation), respectively. Table I provides information about the control polymerizations. The results indicate that the residual styrene monomer content increases while heating the polymers at 240 or 260°. This is more apparent with polymers heated at 260° than with those heated at 240°. This result is likely due to the presence of weak links in the polymer chain. When the weak links break, some depoly-

Figure 2 The vapor–polymer equilibrium partitioning data for styrene in polystyrene versus the temperature and pressure.

Table I   Polymerization Followed by Heating of Styrene Using DtBP as Initiator

Reaction Conditions	Polymer Color	Residual Styrene (ppm)	M_w	M_n	PD
		[Di-t-butyl peroxide] = 1400 ppm			
135°C, 6 h	Clear/colorless	74	225,600	114,100	2.0
Then 260°C, 0.5 h	Clear/colorless	990	178,100	89,900	2.0
Then 260°C, 1 h	Clear/colorless	1480	154,200	82,400	1.9
Then 260°C, 2 h	Clear/colorless	1700	122,000	61000	2
		[Di-t-butyl peroxide] = 1000 ppm			
135°C, 6 h	Clear/colorless	210	264,000	117,000	2.3
Then 240°C, 10 min	Clear/colorless	690	165,000	64,000	2.6
Then 240°C, 20 min	Clear/colorless	890	169,000	70,000	2.4
Then 240°C, 30 min	Clear/colorless	940	154,000	59,000	2.6
Then 240°C, 1 h	Clear/colorless	920	164,000	70,000	2.3

M_w, M_n, weight- and number-average molecular weights; PD, polydispersity.

merization takes place, resulting in the formation of monomer and loss of molecular weight.[12]

Direct Addition of Catalyst

It is extremely difficult to equally distribute trace levels of a catalyst in a viscous polymer melt. Therefore, we chose to add the catalyst to the monomer. However, this also presents a problem because most Friedel–Crafts catalysts also initiate cationic polymerization of styrene. The weight-average molecular weight range of most commercial PS products is between 180,000 and 350,000. The addition of a Friedel–Crafts catalyst to the polymerization process would certainly have a profound effect on the ability to make PS in this molecular weight range. This is because, unless cationic polymerization of styrene is carried out at subambient temperatures, only oligomeric products are formed because of the very high rate of termination. An interesting exception to this generalization makes it worthwhile to consider adding acids at the start of the process: two studies discovered that low concentrations (10–500 ppm) of certain sulfonic acids [e.g., camphor sulfonic acid[13] and 2-sulfoethyl methacrylate (SEM)[14]] catalyze the decomposition of the "Mayo intermediate" that is involved in initiation of spontaneous styrene polymerization. Because the Mayo intermediate is also a powerful chain transfer agent,[15] the reduction of its concentration during styrene polymerization results in a significant

increase of the polymer chain length. Accordingly, it seemed worthwhile to investigate the effect of adding small amounts of SEM on residual styrene levels. We hoped that the level of sulfonic acid needed to catalyze isomerization of the Mayo intermediate during the polymerization might also be enough to catalyze the Friedel–Crafts alkylation of PS by the residual styrene monomer, resulting in a significant decrease of the residual monomer concentration. However, there is a disadavantage to destroying the Mayo intermediate because it enhances the rate of polymerization by reacting with styrene to form initiating radicals. Therefore, when the Mayo dimer is present, the styrene monomer conversion is higher at a given set of polymerization conditions. This effect is apparent in some of the data to be presented.

Polymerizations of styrene containing 50 ppm SEM were conducted using the same conditions employed in the control experiments. The results (Table II) indicate that the presence of SEM results in lower styrene conversions, making it impossible to make a good comparison of the effect (relative to the control) of the acid during subsequent high temperature treatment. However, the data do indicate that SEM does not act as a catalyst to significantly reduce the level of residual styrene in the polymer.

Latent Acid Catalysts

A way to circumvent the problems encountered by adding acid catalysts to the polymerization feed

Table II   Polymerization Followed by Heating of Styrene Using DtBP as Initiator in Presence of 50 ppm SEM

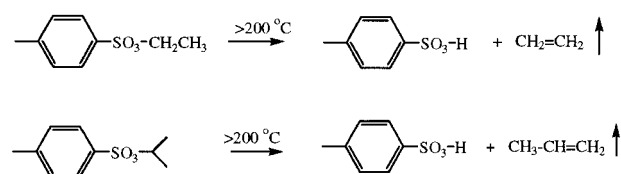| Reaction Conditions	Polymer Color	Residual Styrene (ppm)	M_w	M_n	PD
[Di-*t*-butyl peroxide] = 1400 ppm					
135°C, 6 h	Colorless	435	255,600	130,000	2.0
Then 260°C, 15 min	Colorless	1387	218,100	112,000	1.9
Then 260°C, 30 min	Colorless	1954	194,200	102,200	1.9
Then 260°C, 60 min	Colorless	1538	162,000	81,000	2
[Di-*t*-butyl peroxide] = 1000 ppm					
135°C, 6 h	Colorless	2222	304,000	144,700	2.1
Then 240°C, 15 min	Colorless	2847	265,000	120,500	2.2
Then 240°C, 30 min	Colorless	3121	249,000	113,200	2.2
Then 240°C, 60 min	Colorless	2578	224,000	97,400	2.3

M_w, M_n, weight- and number-average molecular weights; PD, polydispersity.

(i.e., cationic polymerization and interaction with Mayo dimer) while still gaining the advantage of achieving a molecular dispersion of the catalyst in the polymer is to add a latent acid catalyst to the polymerization feed. We chose acid esters that should deesterify at elevated temperatures to form the corresponding acid.

Tosylates

We investigated ethyl tosylate and isopropyl tosylate as precursors of *p*-toluenesulfonic acid. It was presumed that these esters would decompose at elevated temperatures in the manner shown in Scheme 2.

The residual styrene contents in PS prepared by the polymerization of styrene in the presence of ethyl tosylate (1 mol %) initially increased upon heating to 260° but then decreased with time (Table III). After 2 h the residual styrene levels were reduced to a nondetectable level. Isopropyl tosylate is much more effective than ethyl tosylate. The level of residual styrene was nondetect-

able in the PS at the end of the polymerization at 135° and remained nondetectable after heating at 260°, but the polymer molecular weights were higher than those prepared in the control reaction. This indicates that isopropyl tosylate forms *p*-toluenesulfonic acid during the polymerization at 135°. The decrease of the molecular weight with the heating time at elevated temperatures observed in the control reaction was not observed in this reaction. However, the polymer turned brown during the heating process. When the concentration of isopropyl tosylate in the styrene polymerization was reduced to 0.15 mol % with 1000 ppm DtBP initiator, the residual styrene contents were higher than those obtained from a 1 mol % concentration of catalyst but were lower than those obtained in the control reaction.

These results demonstrate that, although low levels of sulfonic acids (<100 ppm) do not act to catalyze the reduction of residual styrene in PS, high levels (<1000 ppm) do significantly reduce the level of residual styrene monomer in PS at 260°. Unfortunately, the high level of sulfonic acid required to remove most of the residual styrene leads to significant polymer discoloration. Furthermore, we are concerned that the high residual level of sulfonic acid left in PS may lead to mold corrosion and other problems.

Evaluation of Phosphorus Compounds

Because sulfonic acids are notorious for generating colored reaction mixtures, it was deemed de-

Scheme 2   The decomposition of the ethyl tosylate and isopropyl tosylate esters at elevated temperatures.

Table III   Polymerization Followed by Heating of Styrene with DtBP in Presence of Tosylate Esters

Reaction Conditions	Polymer Color	Residual Styrene (ppm)	M_w	M_n	PD
[Di-*t*-butyl peroxide] = 1400 ppm, [ethyl tosylate] = 1.0 mol %					
135°C, 6 h	Colorless	360	239,700	113,900	2.1
Then 260°C, 0.5 h	Colorless	540	222,900	110,500	2.0
Then 260°C, 1 h	Light yellow	180	167,100	80,000	2.1
Then 260°C, 2 h	Brown	None detected	160,900	80,900	2.0
[Di-*t*-butyl peroxide] = 1400 ppm, [isopropyl tosylate] = 1.0 mol %					
135°C, 6 h	Light yellow	None detected	273,000	142,600	1.9
Then 260°C, 0.5 h	Light brown	None detected	286,900	150,200	1.9
Then 260°C, 1 h	Brown	None detected	231,200	116,400	2.0
Then 260°C, 2 h	Brown	None detected	258,200	133,900	1.9
[Di-*t*-butyl peroxide] = 1000 ppm, [isopropyl tosylate] = 0.15 mol %					
135°C, 6 h	Colorless	83	286,500	114,800	2.5
Then 260°C, 10 min	Light yellow	280	211,600	85,500	2.5
Then 260°C, 20 min	Light yellow	380	205,800	83,500	2.5
Then 260°C, 30 min	Light yellow	460	196,100	77,800	2.5
Then 260°C, 1 h	Light yellow	500	193,000	76,600	2.5

M_w, M_n, weight- and number-average molecular weights; PD, polydispersity.

sirable to screen other acids. We studied the effect of adding a weaker acid but at higher concentration. Table IV shows the effect of 1% (w/w) of *n*-propylphosphonic acid. It is interesting to note that the extent of monomer conversion during polymerization and the molecular weight loss during high temperature treatment are significantly reduced by the presence of the *n*-propylphosphonic acid. Although the level of residual styrene monomer is significantly reduced during the high temperature treatment, the negative features of *n*-propylphosphonic acid are the high level required and the nontransparent final polymer.

It can be seen (Table V) that various phosphorus acids and their precursors are also effective in lowering residual styrene levels and they do not cause coloration of the resulting polymers. It seems that the activity of the catalysts is related to their acidity or the acidity of acids derived from them. Particularly striking is the high activity of diisopropyl phosphoryl chloride. This may be attributed to the high acidity of the acid that results from thermolysis of the ester groups in this compound or it may be due to HCl being formed. Diphenyl phosphate is also rather effective but it causes the products to be severely discolored when used at higher temperatures and for longer

Table IV   Polymerization Followed by Heating of Styrene Using 1000 ppm DtBP as Initiator in Presence of 1 mol % *n*-Propylphosphonic Acid

Reaction Conditions	Polymer Color	Residual Styrene (ppm)	M_w	M_n	PD
135°C, 6 h	White/translucent	13,420	272,500	112,000	2.4
Then 260°C, 30 min	White/translucent	4,350	247,000	112,000	2.2
Then 260°C, 60 min	White/translucent	3,130	248,000	115,000	2.2
Then 260°C, 120 min	White/translucent	190	241,000	111,000	2.2

M_w, M_n, weight- and number-average molecular weights; PD, polydispersity.

Table V   Polymerization of Styrene with 1000 ppm D*t*BP for 6 h at 135°C and for 20 min at 240°C in Presence of Latent Acids

Catalyst or Catalyst Precursor	Appearance of Product	Residual Styrene (ppm)	M_w	M_n
$(\Phi O)_2P(O)OH$ (0.5 mol %)	Clear and light yellow	100	185,000	77,000
$\Phi P(O)(OH)_2$ (0.1 mol %)	Colorless and transparent	3570	241,000	102,000
$(EtO)_3PO$ (1.1 mol %)	Colorless and transparent	620	248,000	52,000
$(iPrO)_2POCl$ (0.34 mol %) + $(iPrO)_3PO$ (0.16 mol %)	Translucent	38	295,000	131,000
$(iPrO)_2POCl$ (0.68 mol %) + $(iPrO)_3PO$ (0.32 mol %)	Translucent	18	302,000	163,000
$(iPrO)_3PO$ (0.2 mol %)	Translucent	142	169,000	67,400
$(iPrO)_3PO$ (0.1 mol %)	Translucent	615	250,000	123,000
$ClCH_2COOH$ (1.0 mol %) heated for 30 min at 260°C	Colorless and transparent	1210	190,000	80,000

M_w, M_n, weight- and number-average molecular weights.

times. Discoloration in this case is attributed to the phenolic groups present in this compound. Chloroacetic acid was not as effective as the organosulfur or organophosphorus compounds.

CONCLUSIONS

This study demonstrates that residual styrene levels in PS can be lowered by submitting the polymer to acidic conditions at elevated temperatures. The catalysts that are evaluated thus far are not sufficiently reactive to enable this approach to be practical and some of them have the disadvantage that they cause discoloration of the polymer. Further work is needed to find catalysts that are effective at low concentration while leaving the polymer clear and colorless.

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