

Analysis of reactive trace contaminants in styrene by GC/MS

G. Holzer¹, R. Miller², S.L. Hathcock^{3*}, and W. Bertsch³

¹ School of Applied Biology, Georgia Institute of Technology, Atlanta, GA 30332, USA

² Huntsman Chemical Corporation, 5100 Bainbridge Blvd., Chesapeake, VA 23320, USA

³ Department of Chemistry, University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336, USA

SUMMARY

The purity of the styrene monomer is critical since impurities influence the physical properties and appearance of the final polymerized product. It is particularly important to assess the content of the monomer for oxygenated compounds. In this study, two typical monomers were studied. One sample consisted of a one month old monomer that had been exposed to air. The other monomer was a recycle feedstock taken from a continuous polymerization reactor. Analysis was carried out by capillary column gas chromatography/mass spectrometry.

In addition to dimers and trimers that have been reported in the literature, the presence of several classes of oxygenated impurities was established for the first time.

INTRODUCTION

Today, thermal polymerization of styrene is the most common method for commercial polystyrene manufacture. The kinetics of styrene thermal polymerization have been studied by a number of investigators.(1,2) While the exact mechanism of the complex reaction has not been fully established, the reaction scheme proposed by Mayo has generally been accepted.

In the initiation step, styrene dimerizes to form a Diels-Alder adduct. The adduct can then react with an additional styrene molecule to form the initiating species necessary for the polymerization. Styrene trimers are also formed as by-products of this reaction. Under the conditions employed to polymerize styrene thermally, styrene dimers such as 1,2-diphenylcyclobutane are generated. The formation of dimers and trimers during styrene thermal polymerization is therefore inevitable, with their concentrations dependant on the polymerization temperature.

The purity of styrene monomer is usually established by gas chromatography. The chromatographic conditions are selected to resolve the major impurities which consist mainly of alkylated benzenes and -methyl styrene. Polymerization grade monomer is usually better than 99.8% pure. Monomer stabilized with 10-25 ppm of the polymerization inhibitor tertiary butylcatechol may be 1-5 weeks old, prior to polymerization. It is usually shipped and stored at temperatures not to exceed 65°C. At temperatures around 20°C, dimeric and trimeric styrenes are formed at a rate of 30-40 ppm per day. The production of these oligostyrenes is also accompanied by the generation of oxygenated derivatives and occasionally the development of a yellow color. The cause of this discoloration is not fully

*To whom correspondence should be addressed

understood. It is common practice in the industry to routinely assay finished polymers for their dimer and trimer content. This is important as these compounds influence the melt/flow characteristics of the resins through a plasticizing effect. High oligomeric contents can also promote yellow discoloration under certain conditions. Although the chemistry of oligostyrenes has been extensively studied, little information on thermal stability or oxidation products is available. The structure of certain species of dimeric styrenes has been well elucidated but the identity of the trimeric isomers is less well known.

Due to the influence that these components exert on product quality it was decided to undertake a detailed analysis of oligomeric fractions of styrene that are typically found in a production environment. GC/MS was chosen as the analytical tool even though very few structures of the expected compounds have been reported in the literature. We were particularly interested in the oxygenates as possible polymerization inhibitors or the source of color bodies. The two samples that were selected for analysis were (i) a production grade monomer, aged at 22 °C for one month, and (ii) a recycle feedstock that had undergone circulation through a commercial continuous polymerization reactor.

EXPERIMENTAL

The styrene samples were used without additional workup. Analysis was performed by GC and GC/MS. GC was done on a HP 5890 instrument, equipped with FID and split/splitless/cold on-column inlets. The column was a fused silica capillary, 50 m x 0.21 mm i.d., coated with methylphenylpolysiloxane (HP 5, d_f 0.33 μ m, Hewlett Packard, Avondale/PA). A second column, 50 m x 0.25 mm i.d., coated with methylpolysiloxane (CP-Sil-5 CB, Chrompack, Raritan/NJ) was also used. GC/MS was carried out on a HP 5970 instrument (Hewlett Packard, Avondale/PA), using the same column type as above except that it was 12 m in length. Flow rates were adjusted to approx. 35 cm/sec, using helium as carrier gas. The mass spectrometer was scanned from 35-450 amu, using standard EI condition. The scan rate was 1.2 seconds/scan.

RESULTS AND DISCUSSION

The analytical problem is formidable, due to several factors. The impurities are present only at the trace level and some components are thermally labile and reactive. Information in the literature of physical properties of suspected components is sparse. Since isomers are known to exist, chromatographic efficiency must be high. Mass spectrometry is not specific enough for the determination of structural isomers. In addition, hydroxylated or polar species require well deactivated columns.

Since polymerization is carried out by thermal treatment of the monomer, temperature settings in the GC are important.⁽³⁾ Thermal stress should obviously be minimized, especially during sample introduction. Figure I shows that artifact formation is severe when the sample is exposed to high inlet temperatures. Cold on-column injection, Figure II, is obviously preferred.

Figure III shows a chromatogram of the recycle product that has been thermally exposed. The product is yellow in color and obviously contains a significant level of impurities. Some of the compounds have been tentatively identified by their mass spectra, or by comparison with standard compounds, as listed. Attempts to carry out silanization of this sample produced an extremely complex pattern that was beyond the scope of this investigation. Derivatization should not be ruled out in future studies. Components that do not react with the derivatization agents can easily be identified and the information can be used to rule out certain structures.

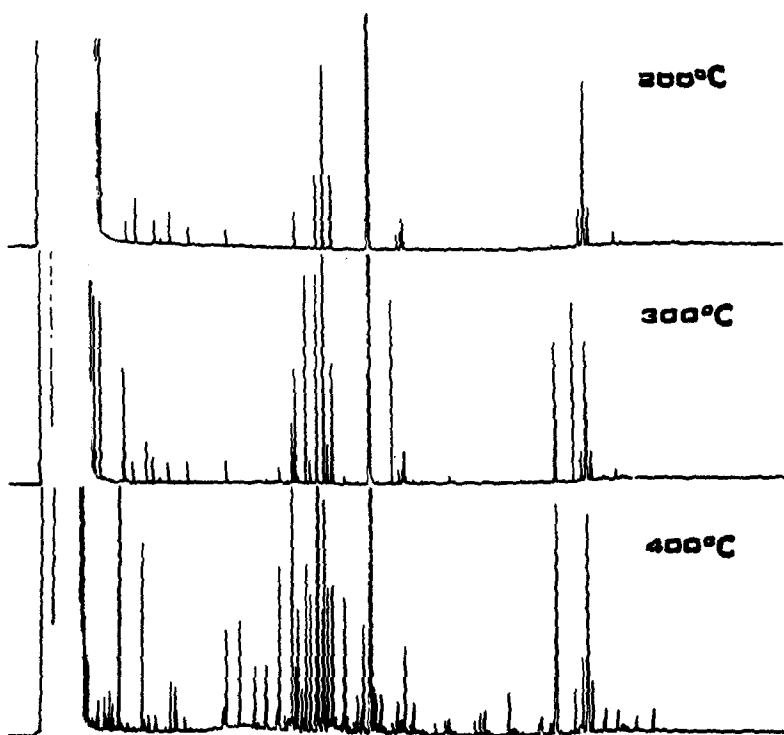


Figure I. Artifact formation from thermal exposure of a styrene monomer, splitless injection. For conditions, see text.

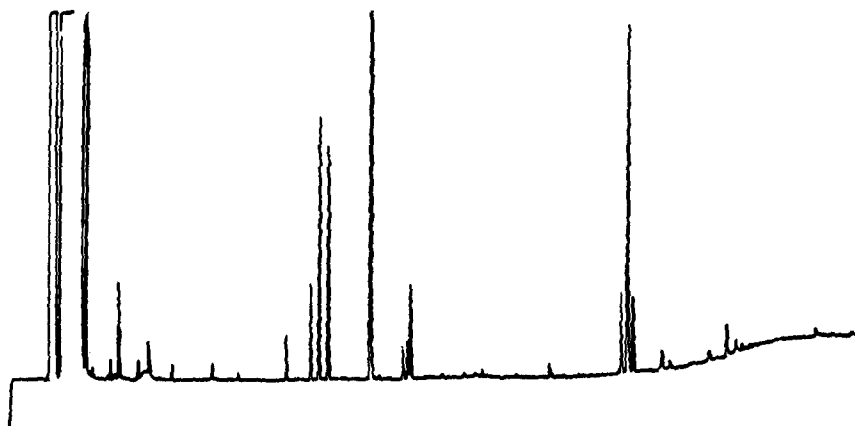


Figure II. Styrene monomer by cold on-column injection. Chromatographic conditions as in fig. I.

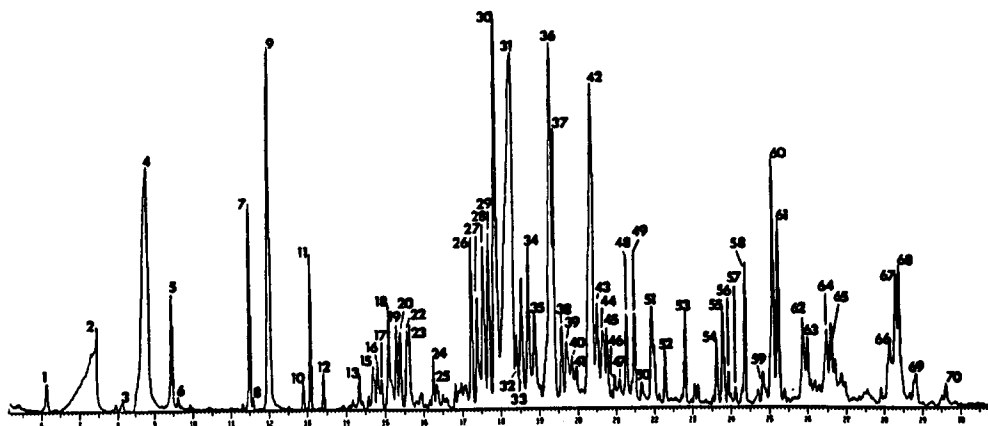


Figure III. Impurities in a styrene monomer from a recycle process.

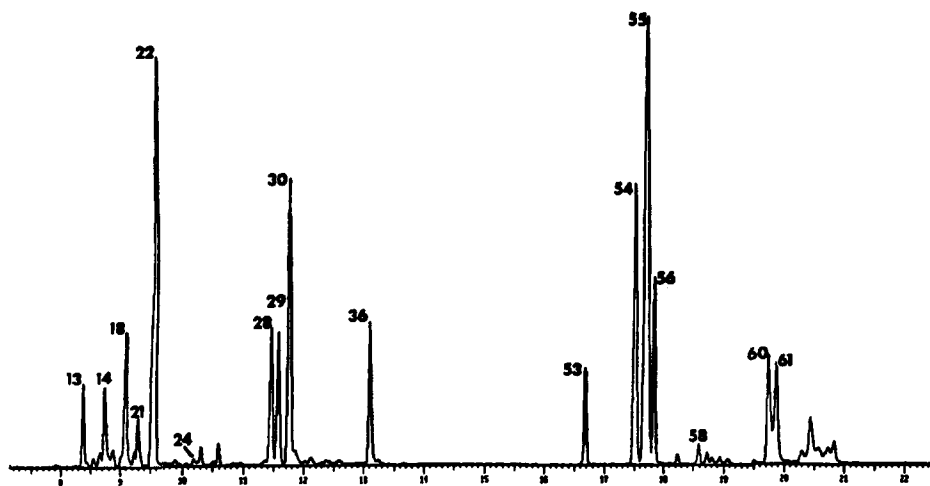


Figure IV. Impurities in a thermally aged styrene sample. For substance identification, see text.

The profile of the thermally aged styrene sample is shown in Figure IV. A list of identified compounds is shown in Table I. It should be noted that not all substances appear in both chromatograms. The compounds were identified by interpretation of their mass spectra. Mass spectra of some styrene isomers are shown in figure IV.

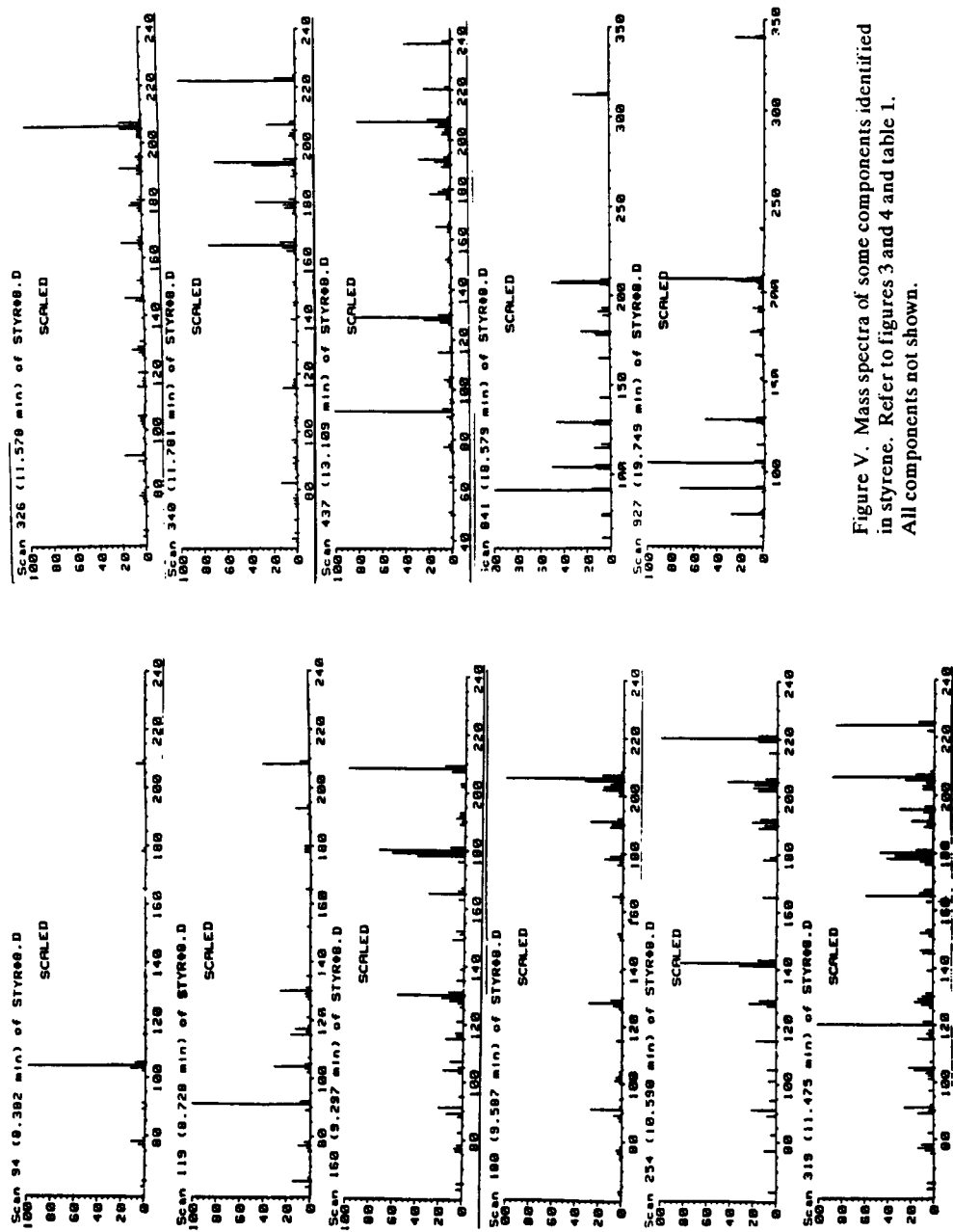


Figure V. Mass spectra of some components identified in styrene. Refer to figures 3 and 4 and table 1. All components not shown.

TABLE I
Impurities in Styrene

Peak Number	Compound	Peak Number	Compound
1	Unknown	25	Styrene dimer with three unsaturations
2	Benzoic acid	26	Diphenylhydroxy butene isomer
3	Phenylacetic acid	27	Diphenylhydroxy butene isomer
4	1-Phenyl-1,2-dihydroxyethane (styrene glycol)	28	Diphenylhydroxycyclobutane isomer*
5	Hydroxy phenyl acetaldehyde	29	Diphenylhydroxybutene isomer*
6	C ₅ -alkyl phenol	30	Diphenylhydroxybutadiene isomer
7	Methyl dimethoxyphenyl ketone or C ₄ -alkyl-methoxyphenol	31	Hexadecanoic acid
9	4-tert Butylcatechol	32-35	Unknown
10	Diethylphthalate	36	Diphenylhydroxymethylbutene isomer
11	Unknown	37	Unknown
12	Unknown	38	Diphenylhydroxymethylcyclobutane isomer
13	cis-1,2-Diphenylcyclobutane	39	Diphenylhydroxymethylcyclobutane isomer
14	1,3-diphenyl-butene*	40-41	Unknown
15-17	C ₉ -alkyl phenol	42	Octadecanoic acid
18	trans-1,2-Diphenylcyclobutane	43-51	Unknown
19	C ₁₀ -alkyl phenol	52	Tolylphenylhydroxyethylbutene
20	Ethyl propylphthalate	53	1,3,5-Triphenylhexene
21	1,2-Diphenylbutene*	54-57	Styrene-trimer-isomers*
22	1,2-Diphenylbutadiene	58	1,3,5-Triphenylhexane
23	Tetradecanoic acid	59	Unknown
24	Tolylphenylbutadiene*	60-63	C ₂ -alkyl styrene trimers*
		64-70	Unknown

* Standards or library mass spectra were not available to verify the proposed structure.

The mass spectrum 13 shows a major fragment at m/z 104 and a molecular ion at m/z 208. The compound was identified as cis-1,2-diphenylcyclobutane, by comparison with a standard. The trans-1,2-diphenylcyclobutane isomer, compound 18 has a similar mass spectrum, as expected. It is interesting that these substances have a significant difference in the expected boiling points, even though the melting points differ by only 2-3 degrees.(4,5) Gross et al.(6) have studied stereochemical effects on the mass spectra of the two isomers in detail. The differences in mass spectra are slight, even under low energy EI ionization conditions. They report an unusual rearrangement or an unusual concerted elimination for the cis-isomer. Cis-1,2-diphenylcyclobutane has been reported to thermally rearrange, however at 250°C only the more stable trans-isomer is observed, but the major product is styrene.

The fragmentation pattern of peak 14 suggests an open chain butene structure. The ion at m/z 91 is the most intense fragment, which requires that a benzyl-group is part of the molecular structure. The formation of the tropylium ion and the peaks of m/z 105 and M-15 are in agreement with a 1,3-diphenylbutene structure. The high degree of fragmentation of compound 21 suggests an open chain butene structure (M^+ 208). The peak at m/z 180 is formed by the loss of ethene. The peak at m/z 130 is formed by the loss of benzene, producing a fully conjugated molecule. This fragmentation pattern is best explained by a 1,2-diphenyl substituted butene. The mass spectrum of compound 22 is similar to the spectrum of compound 21, except that the major fragment and the molecular ion are shifted to lower masses by 2 amu. This suggests an open chain diphenyl substituted butadiene structure.

The major peaks in the mass spectrum of compound 24 are shifted to higher masses by 14 amu, compared to compound 22. The intense fragment at m/z 142 (M^+ -benzene) and the molecular ion M^+ 220, suggest an open chain butadiene structure. The peak at m/z 128 (loss of toluene) indicates that one of the benzene rings is substituted with a methyl group, in favor over a methyl branch in the open chain. The cluster of peaks around $M-28$ (loss of ethene) suggests a 1,2-tolyl-phenyl-substituted butadiene.

The mass spectra of compounds 26 and 27 are similar. The molecular ion of m/z 224 and $M-31$, $M-45$ peaks suggest an oxygenated styrene dimer structure.

The mass spectrum of compound 28 shows a molecular ion at m/z 224 and a peak at M^+-18 , suggesting a hydroxylated styrene dimer. The most intense fragment (m/z 120) is formed by the loss of styrene from the parent molecule, a rearrangement reaction which is favored in the cyclobutane structure. The high intensity of the $M-18$ peak suggests that the hydroxyl group is not bonded to one of the benzene rings because phenolic OH-groups have generally a low tendency to be eliminated as water. Thus compound 28 consists most likely of a diphenyl-substituted hydroxy-cyclobutane.

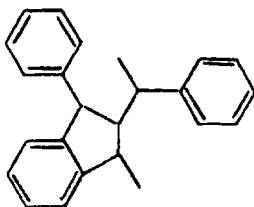
The mass spectrum of compound 29 is similar to the spectrum of compound 22, for which a 1,2-diphenylbutadiene structure was proposed. The most intense fragment (m/z 206) is formed by elimination of water from the parent molecule. The ion subsequently fragments into daughter ions, producing a mass spectrum similar to compound 22. Thus compound 29 is most likely an open chain diphenyl-substituted butene. Because of the strong M^+-18 peak, the hydroxyl group is most likely attached to the butene portion of the molecule, which makes compound 29 an open chain isomer of compound 28.

Compound 30 has a molecular ion of m/z 222 and intense fragments at m/z 194 (M^+-18) and m/z 165. The fragment of m/z 165 was observed in all mass spectra of styrene dimers and is characteristic for this class of compounds. The molecular mass suggests an oxygenated styrene dimer as likely structure for compound 21.

The mass spectrum of compound 36 shows a molecular ion of m/z 238, indicating a substituted styrene dimer. The peaks at M^+-18 , M^+-31 and M^+-46 point to the presence of a primary OH-group. Since there is no evidence for hydroxytropylium ions, the hydroxymethyl function is most likely attached to the butane moiety of the molecule. The strong peak of m/z 129, formed by the elimination of benzene from the M^+-31 ion and the tropylium ion (m/z 91) provide additional support for a hydroxymethyl substituted styrene dimer as structure for compound 36.

Compound 53 was identified by comparison with a standard as 1,3,5-triphenylhexene, the linear styrene trimer. The mass spectral fragments of the compound are formed by successive cleavage of the carbon-carbon bonds of the hexene chain.

The mass spectra of components 54, 55, 56 and 57 are very similar, showing only three principal fragments at m/z 91, 129 and 207. Molecular ions are not present, except for compound 57, which shows a peak at M^+-312 . The ion at m/z 207 is formed by the loss of a terminal styrene unit from parent molecule. The ion decomposes further by elimination of benzene to m/z 129. A possible structure for one of the isomers is shown below.



The mass spectrum of component 58 shows a molecular ion of M^+ -314 and peaks at m/z 209, 194, 105 and 91. This fragmentation pattern is expected from a 1,3,5-triphenylhexane.

Compounds 60, 61, 62 and 63 have similar mass spectra. The molecular ion at m/z 340 is shifted to higher masses by 28 a.m.u. compared to the styrene trimer. The enhanced ions at m/z 105 and 91 suggest an alkyl substitution on one of the benzene rings. The fragments of m/z 207 and m/z 129 are similar to those expected from the degradation of styrene trimers with structures similar to those proposed for components 54-57.

A great deal of information is available in the literature on styrene polymerization. Much of the work is concerned with mechanistic effects and is carried out in the condensed phase. Photochemical studies are also abundant, but little is known about the gas phase chemistry of styrene. The use of deuterated intermediates would be helpful for further examination of such thermally induced processes.

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