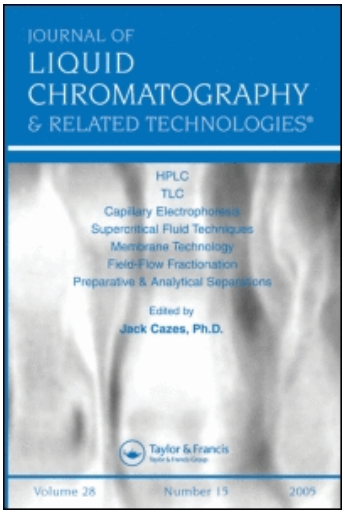

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CHARACTERIZATION OF INHIBITORS IN VINYL AND ACRYLIC MONOMERS

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ABSTRACT

Hydrogen bonding favorably influences the size exclusion separation of trace levels (mg/L) of a phenolic inhibitor from a vinyl or an acrylic monomer. The sizes of phenolic compounds such as p-tert-butyl catechol, hydroquinone, and hydroquinone monomethyl ether are increased by interactions with the THF mobile phase. Since most common monomers such as vinyl acetate, methyl methacrylate, and styrene do not have hydroxyl functionality, their size separations from monohydroxyl inhibitors is nearly two minutes and from dihydroxy inhibitors by close to three minutes. Use of a diode array detector allows identification of the inhibitors, monomers, and impurities via UV spectra and chromatograms.

INTRODUCTION

Although size exclusion chromatography (SEC) is primarily used for studies of molecular weight distributions of polymers, small pore size SEC columns can provide efficient separations of small molecules. Plastisizers and antioxidants are examples of low molecular weight additives that can be readily isolated

from polymers using small molecule SEC.[1] Monomers also contain additives such as inhibitors that can be studied by SEC. This paper describes the use of small molecule SEC and a diode array detector to characterize the inhibitors in vinyl and acrylic monomers.

Warren and his co-workers[2] have described how the size and retention of small molecules can be altered by the use of different mobile phases for small molecule SEC. They illustrated the solvent effect of the mobile phase with two examples. The first example was the comparison of the retention of octanol and octanediol in two different solvents. Octanol and octanediol have nearly the same molecular size and overlapping peaks from small molecule SEC columns when chloroform is the mobile phase. If THF is the solvent, octanediol elutes first and is completely separated from octanol due to the different hydrogen bonding capabilities of the two alcohols. The two hydroxyl groups of octanediol provide greater hydrogen bonding interactions and greater molecular size than octanol in THF.

The other example from Warren and coworkers is the small molecule SEC of butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). They show that BHT is a larger molecule and can be completely separated from BHA if the solvent is chloroform. The separation in chloroform can be explained by looking at the structures of the molecules in Figure-1. BHT has two bulky t-butyl groups on an aromatic ring while BHA has only one t-butyl group. Both compounds have larger size and elute earlier in THF versus chloroform, however, BHT experiences less hydrogen bonding because

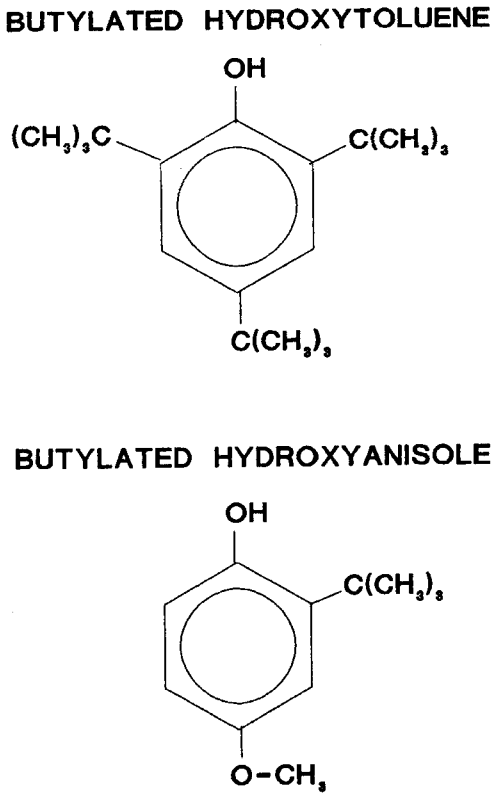
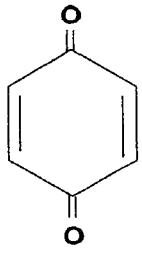


FIGURE 1. Structures of BHT and BHA.

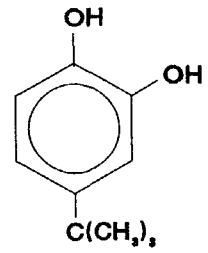
of the t-butyl groups on both sides of the hydroxyl. Therefore, BHT and BHA have similar size and are not separated when the solvent is THF. Since this paper also involves the study of phenolic and quinone type compounds, the solvent effect also has a major impact on the small molecule SEC of inhibitors.

The inhibitors that are involved in this study are p-tert-butyl catechol (TBC), hydroquinone, hydroquinone monomethyl ether, and benzoquinone. Figure-2 shows the

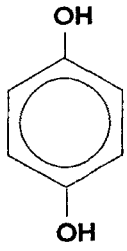
BENZOQUINONE



p-t-BUTYL CATECHOL



HYDROQUINONE



HYDROQUINONE MONOMETHYL ETHER

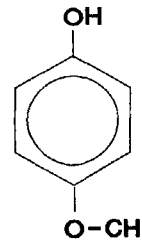


FIGURE 2. Structures of inhibitors.

structures of these inhibitors, which are commmonly used in vinyl and acrylic monomers. Since TBC and hydroquinone would both have two hydroxyl groups, these phenolic type compounds are larger molecules than benzoquinone when the solvent is THF. Hydroquinone monomethyl ether has one hydroxyl group, and it would be expected to elute between hydroquinone and benzoquinone. Because of the bulky t-butyl group of TBC, the retention time of TBC should also be earlier than the hydroquinone. Most vinyl and acrylic monomers

also have no hydroxl groups and smaller size than the inhibitors. Therefore, complete chromatographic resolution of an inhibitor and a monomer should be expected using small molecule SEC with THF as the mobile phase.

Another important tool for the characterization of an inhibitor in a vinyl or acrylic monomer is a diode array detector (DAD). A DAD can not only simultaneously acquire chromatograms at several wavelengths, but it can also be programmed to obtain complete UV spectra throughout one SEC run. The major advantage of the wealth of UV data is to resolve overlapping chromatographic peaks. An inhibitor can then be identified and its purity can be assesed via the UV spectra and chromatograms. The amount of inhibitor is quantified by integration of a chromatogram at a wavelength where the sensitivity is greatest and there is no absorbance from other compounds.

The analysis of vinyl or acrylic monomers for the inhibitor is necessary to insure safe bulk storage. If the free radical polymerization of these monomers is not prevented during storage, the very rapid and exothermic reaction could produce an explosion and fire. The inhibitor reduces the possibiltiy of a catastrophe, beause it acts as a scavenger for free radicals. When conditions are right for the production of free radicals, the inhibitor will eventually be used up.[3] Therefore, the status of the inhibitor should not only be determined on arrival of a new shipment of monomer, but also at regular intervals during storage.

Colorimetric and UV-visible spectroscopic methods for the inhibitor analysis can be found in the

literature[4,5], but these methods have several limitations. The colormetric method can not be used to detect many phenolic inhibitors such as TBC, and both methods require the analyst to handle large amounts of a hazardous monomer. GC or GC/MS could be used to determine the inhibitor[6], but high molecular weight polymerization products can not be detected with a GC. Reverse phase HPLC could be used, but a strong sovent would have to be used to flush polymer from the column after each run. On the other hand, small molecule SEC and the DAD provide the capabilities to determine both the condition of the inhibitor and the presence of polymer.

EXPERIMENTAL

Equipment and Conditions

The modular SEC system was assembled to have the flexibility of changing components for different applications. A Waters model 510 pump (Waters Chromatography Div., Millipore Corp., Milford, Massachusetts) was used to deliver the tetrahydrafuran (HPLC grade THF from Baxter, Burdick & Jackson Div., Muskegon, Michigan) at 0.9 ml/minute. 0.2 ml of samples and standards were injected with a Waters U6K injector. Two 10 μ Phenogel (Phenomenex, Torrance, California) 300 X 7.8 mm columns were selected for this study. The first column has packing with 100 Å pore size , while the packing in the second column has 500 Å pore size. The molecular weight exclusion limits of the 100 and 500 Å columns are 50-1000 and 500-10,000 respectively. Columns with smaller particle and pore sizes could provide greater efficiencies than these 10 μ columns, but they were selected to be used for many applications.

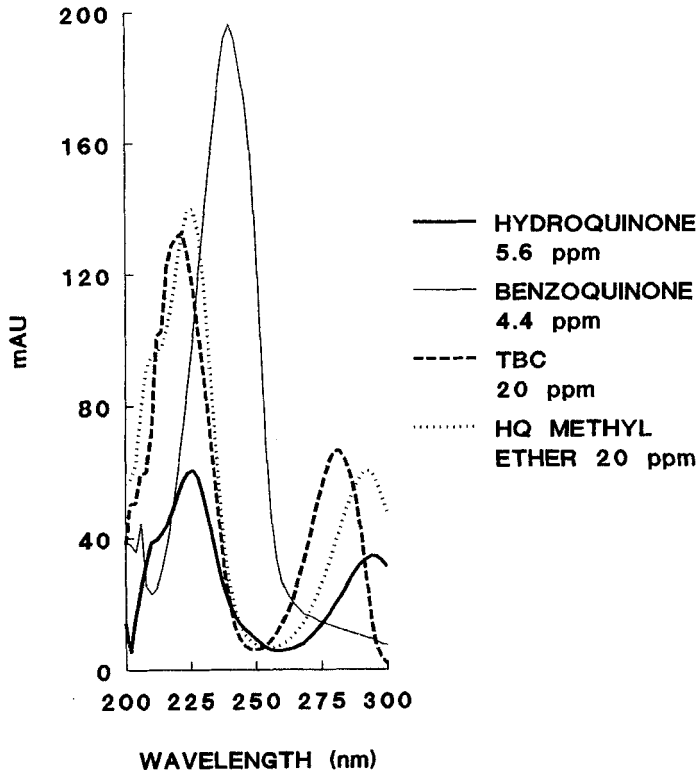


FIGURE 3. UV spectra of inhibitors.

The eluents from the columns were analyzed using a HP 1040A diode array UV detector (Hewlett Packard, Palo Alto, California). The data was acquired and stored through communications with a HP 9000 computer and a HP 35900A 10 mega byte hard disk. The detector was programmed to acquire chromatograms at 214, 220, 230, 240, 250, 260, 280, and 300 nm. Complete UV spectra were also saved every 2 seconds during each run.

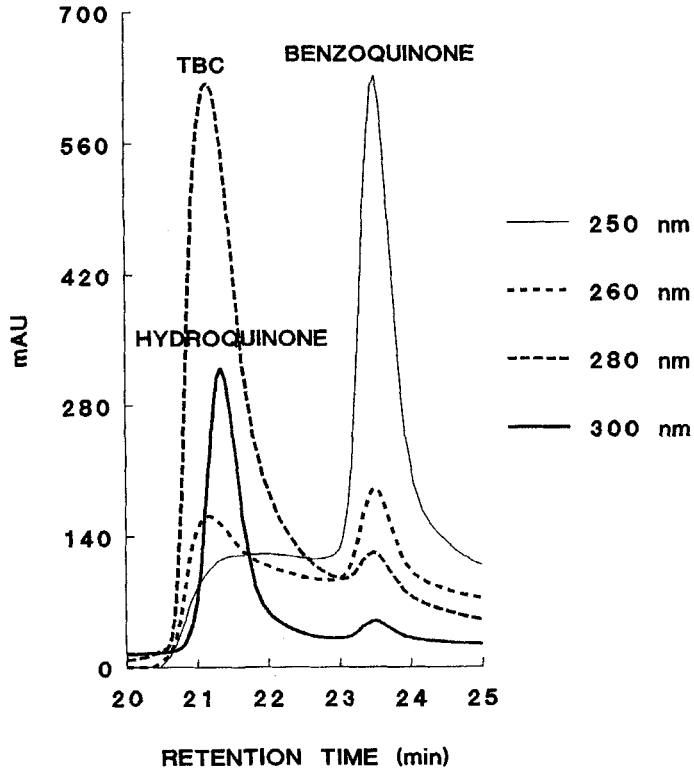


FIGURE 4. Chromatograms of mixture.

Standards and Samples

Many standards were prepared in THF to study the small molecule SEC of inhibitors and monomers. TBC, hydroquinone, hydroquinone monomethyl ether and benzoquinone were each run individually, and a mixture of 200 ppm TBC, 60 ppm hydroquinone, and 20 ppm benzoquinone was injected to examine the resolution of these inhibitors. Data was also acquired from another solution of 176 ppm hydroquinone monomethyl ether and

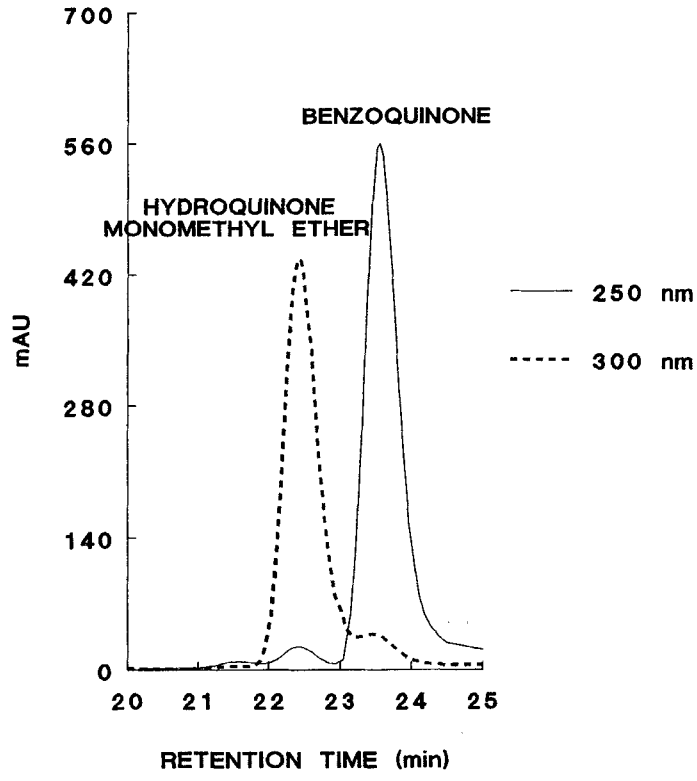


FIGURE 5. Chromatograms of mixture 2.

20 ppm benzoquinone. The separation of styrene monomer and TBC was characterized with a sample containing 12.5 ppm styrene and 100 ppm TBC. A solution of 300 ppm methyl methacrylate and 20 ppm of benzoquinone was also injected to see if this combination of monomer and inhibitor could be resolved.

Other samples and standards were prepared to pursue the trace amounts of inhibitor that are added to

monomers for storage. A vinyl acetate sample was prepared by adding one ml of the monomer to one ml of THF. A series of methyl methacrylate solutions were run to determine the detection limit of benzoquinone in methyl methacrylate. 1:1 dilutions in THF of a laboratory styrene sample and a bulk storage styrene sample were run, and standards containing 10, 20, 40, 60, 80, and 100 ppm of TBC were prepared to determine TBC in Styrene. After aging the 100 ppm standard for one week, it was run again to characterize oxidized inhibitor.

RESULTS AND DISCUSSION

Separation and Identification of Inhibitors

Small molecule SEC and the DAD provide resolution and identification of TBC, hydroquinone, benzoquinone, and hydroquinone monomethyl ether. Figure-3 has the UV spectra that were acquired at the peaks in the individual runs of the inhibitors. The differences in the spectra are not only useful for the identification of the inhibitors, but the spectra are also used to select appropriate wavelengths for chromatograms. For example, Figure-4 shows that hydroquinone is resolved from TBC in the chromatogram at 300 nm. The curves of the mixture in Figure-4 are some of the chromatograms that were acquired in one SEC run. The wealth of data from chromatograms and spectra enable complete characterization of the mixture.

The number of hydroxyl groups in the structure has the most significant influence on SEC retention of an inhibitor in THF. Hydroquinone and benzoquinone have almost the same molecular weight, but the molecules

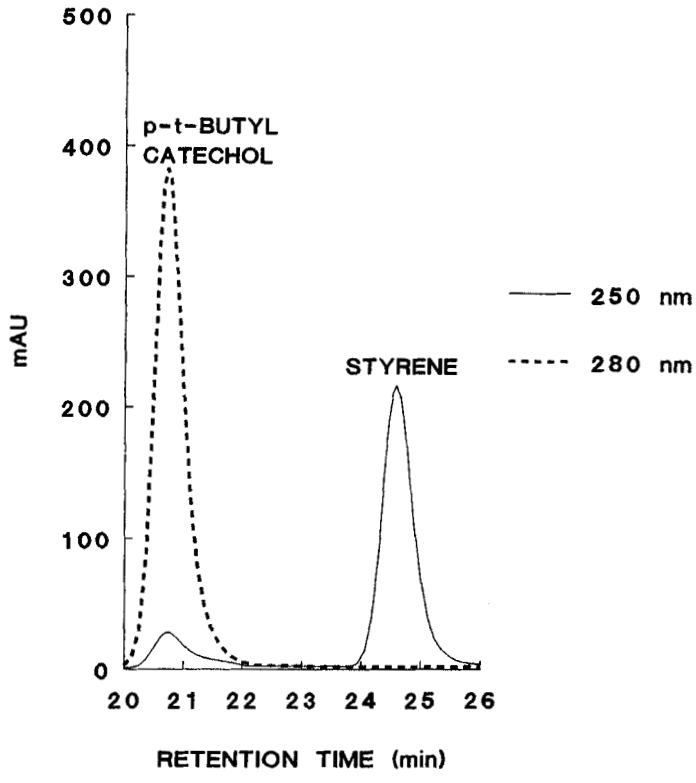


FIGURE 6. SEC of styrene and TBC.

have very different size in THF because hydroquinone has two hydroxyls while benzoquinone has no hydroxyls. This size and retention difference is indicated by the two minute separation of benzoquinone and hydroquinone in Figure-4. TBC and hydroquinone both have two hydroxyls and overlapping peaks in Figure-4. The bulky t-butyl group of TBC provides only a slightly earlier elution time than hydroquinone. Figure-5 displays the separation of benzoquinone and hydroquinone monomethyl

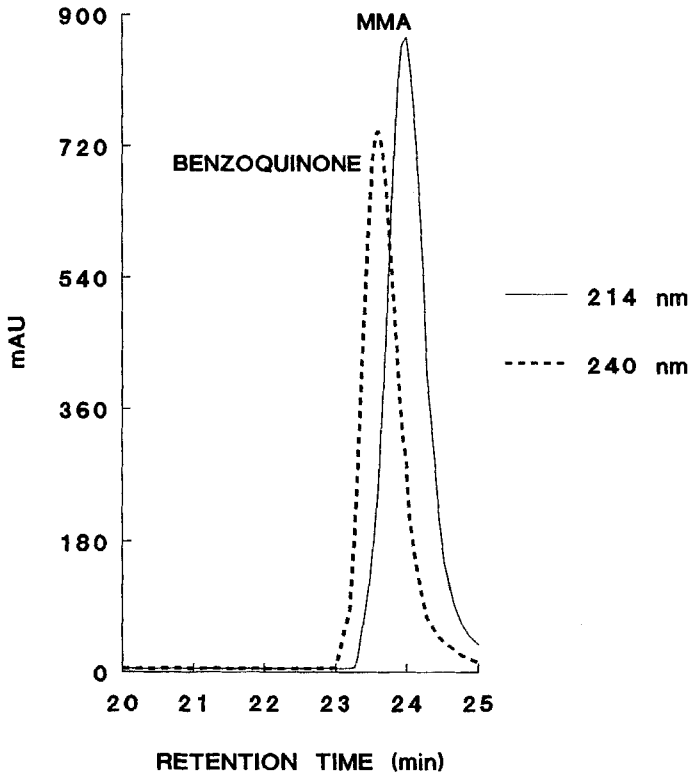


FIGURE 7. SEC of methyl methacrylate.

ether. Since hydroquinone monomethyl ether has one hydroxyl group, its elution time is almost exactly between hydroquinone and benzoquinone.

Since most common vinyl and acrylic monomers are small molecules and do not have hydroxyls, it is easy to separate a phenolic type inhibitor from a common monomer. Figure-6 illustrates the very good resolution of TBC and styrene. Hydroquinone and hydroquinone monomethyl ether also are easily resolved from small

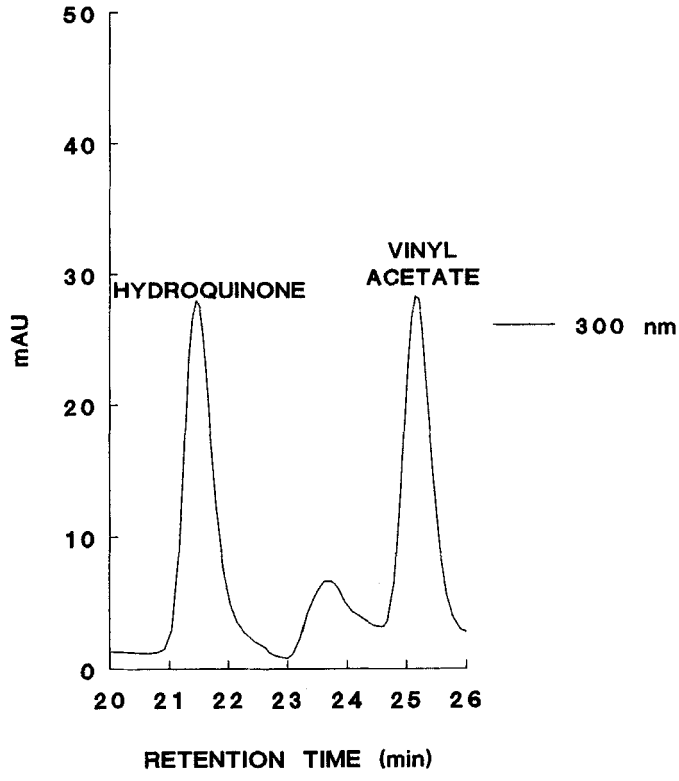


FIGURE 8. Detection of inhibitor in vinyl acetate.

monomers such as butyl acrylate, methyl methacrylate, vinyl acetate, and styrene.

Because benzoquinone has no hydroxyls, its elution time is very close to the common small monomers. However, the benzoquinone peak can be resolved from monomers using the chromatograms and spectra from the DAD. Figure-7 demonstrates how bezoquinone and methyl methacrylate peaks can be separated using chromatograms

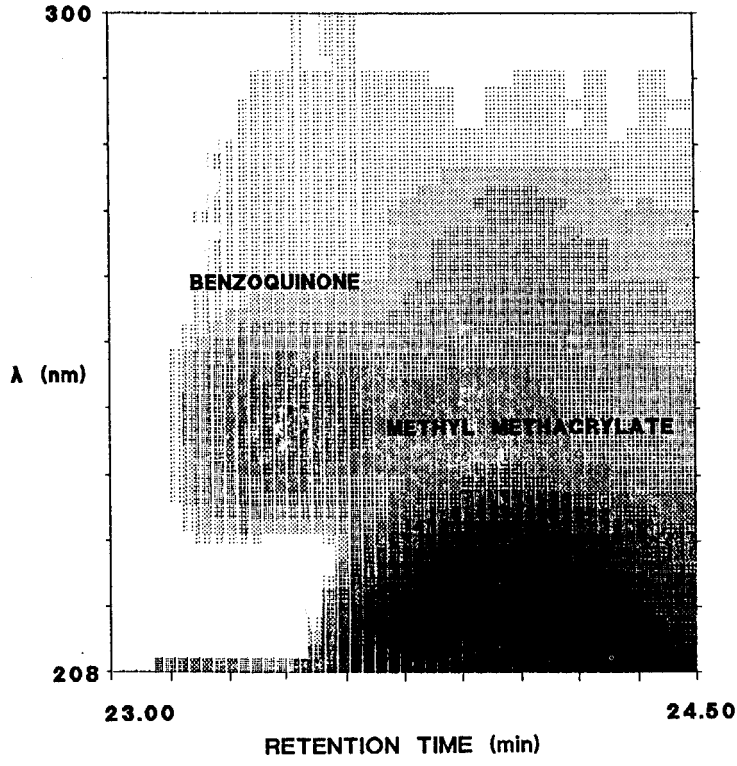


FIGURE 9. Detection of benzoquinone in MMA.

at 214 nm and 240 nm. Overlapping styrene and benzoquinone peaks can also be resolved with the UV data.

Other monomers that have higher molecular weight and hydroxyl functionality could have similar SEC retention to the phenolic type inhibitors. An example would be hydroquinone monomethyl ether and hydroxy ethyl methacrylate which both have one hydroxyl group. This combination of inhibitor and monomer could be

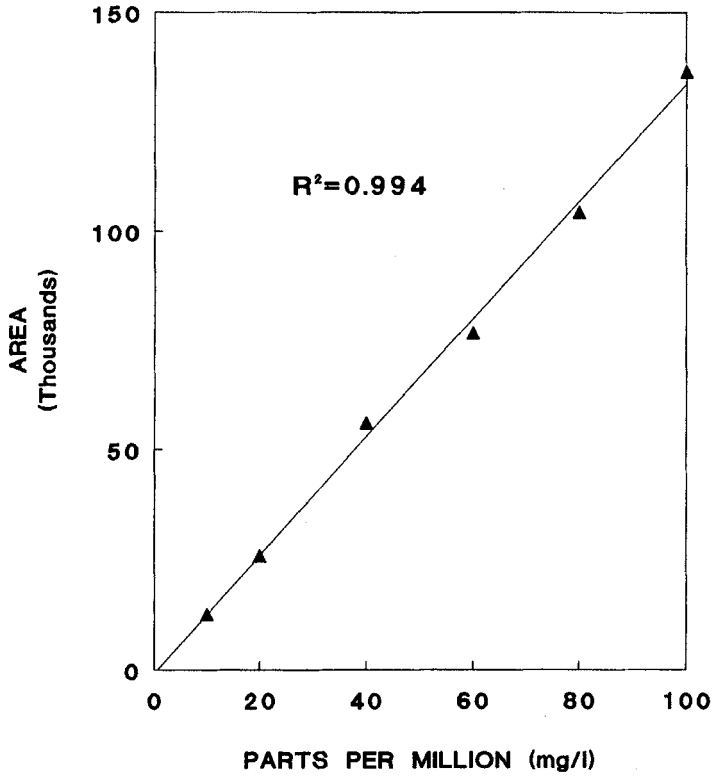


FIGURE 10. Calibration curve for p-t-butyl catechol.

resolved using chromatograms at 214 nm and 300 nm. In cases where the UV spectra of an inhibitor and a monomer are similar, curve resolution software could be used to characterize the components.[7]

Detection of Inhibitors in Monomers

Only trace amounts of inhibitors are actually added to monomers for storage. Figure-8 demonstrates that trace amounts of hydroquinone can be detected in

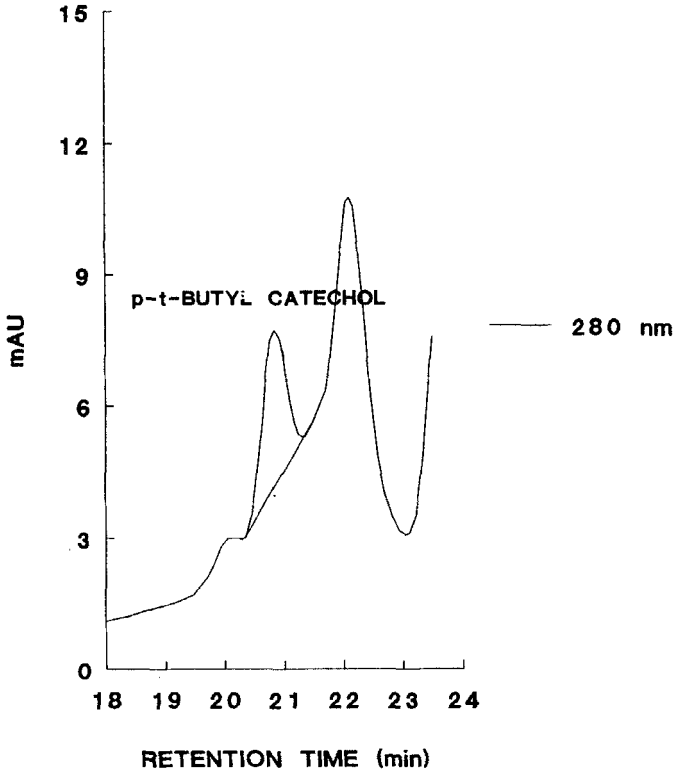


FIGURE 11. SEC of a styrene sample.

vinyl acetate. However, parts per million levels of benzoquinone are hidden by the high absorbance of a concentrated monomer. If methyl methacrylate monomer is diluted to 0.1% in THF, then a 5% concentration of benzoquinone in the monomer can be detected. The UV data from 5% benzoquinone in methyl methacrylate is illustrated in the isogram of Figure-9. It is also difficult to detect benzoquinone in concentrated styrene, but columns with 5μ particle size and 50Å pore

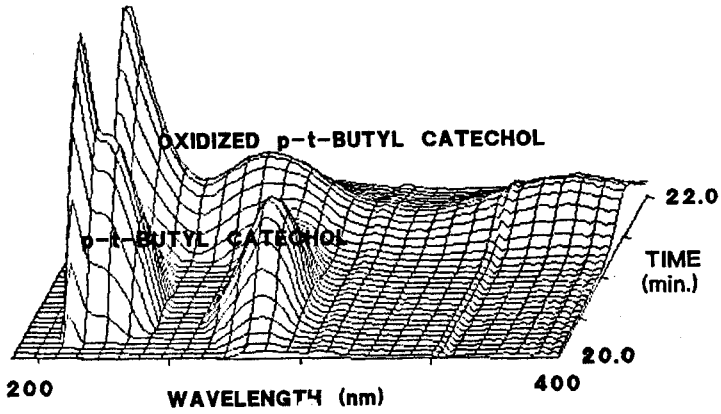


FIGURE 12. SEC of oxidized p-t-butyl catechol.

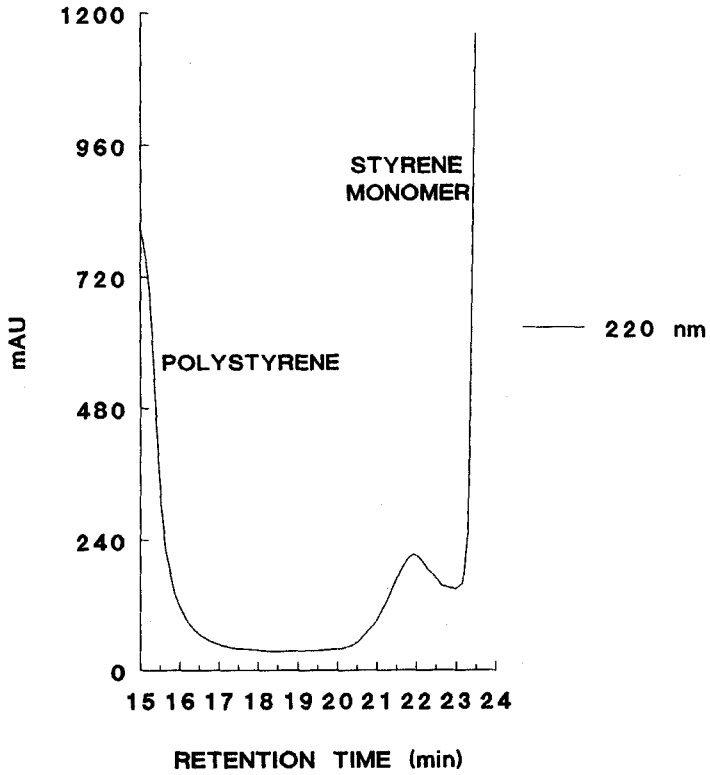


FIGURE 13. SEC of styrene sample 2.

size may provide better resolution of benzoquinone and monomer.

Since the separation of TBC and styrene is close to three minutes, this combination is a good example for quantitative analysis of the inhibitor. The calibration curve at 280 nm for TBC in Figure-10 provides a linear equation for determinations of the inhibitor in styrene samples. TBC in styrene sample-1 (Figure-11) is identified by a spectrum at 21 minutes, and from the calibration curve this sample contains 12 parts per million of the inhibitor. Hydroquinone and hydroquinone monomethyl ether would easily be determined in momomers using 300 nm chromatograms of standards and samples.

The combination of SEC and the DAD also allows the detection of oxidized TBC and polymer in styrene. Data from a one week old TBC standard is shown in a 3D plot in Figure-12. The oxidized inhibitor elutes earlier because of the loss of hydroxyl functionality. Evidence of polystyrene in Figure-13 shows that polymer is easily identified with this method. SEC and the DAD are useful for characterization of both the inhibitor and impurities in monomers.

FUTURE WORK

Future small molecule SEC studies will involve surfactants. Since many surfactants have hydrogen bonding capabilities they should also have interesting small molecule SEC retention.

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