Dr. E.J. Parks
x2040

Div. 561

NBSIR 82-2577

Advances in the SEC Characterization of Organometallic Copolymers and Copolymerization: Desorption of Charged Species by Injected Dilute Acetic Acid

---

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Materials Chemistry Division
Washington, DC 20234

August 1982

Prepared for
David Taylor Naval Ship R & D Center
Annapolis Laboratory
Annapolis, MD 21402

NBSIR 82-2577

ADVANCES IN THE SEC CHARACTERIZATION OF ORGANOMETALLIC COPOLYMERS AND COPOLYMERIZATION: DESORPTION OF CHARGED SPECIES BY INJECTED DILUTE ACETIC ACID

E. J. Parks, R. B. Johannesen, and F. E. Brinckman

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Materials Chemistry Division
Washington, DC 20234

August 1982

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared for
David Taylor Naval Ship R & D Center
Annapolis Laboratory
Annapolis, MD 21402

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

TABLE OF FIGURES (CAPTIONS)

ADVANCES IN THE SEC CHARACTERIZATION OF ORGANOMETALLIC COPOLYMERS AND COPOLYMERIZATION: DESORPTION OF CHARGED SPECIES BY INJECTED DILUTE ACETIC ACID

E. J. Parks, R. B. Johannesen, and F. E. Brinckman

Materials Chemistry Division
National Bureau of Standards
Washington, DC 20234

SUMMARY

The chemical characterization of controlled-release, biocidal triorganotin-containing copolymers (organometallic polymers, OMPs) is necessary for predicting the in-service performance of these important materials. An OMP investigated in the present research was prepared by the free radical copolymerization of tributyltin methacrylate (TBTM) and methyl methacrylate (MMA). Size exclusion chromatography (SEC) on μStyragel, coupled with an in-line graphite furnace atomic absorption detector (GFAA) quantitates the bioactive tin in at least two well-resolved fractions: a polymer fraction, and, probably, unreacted TBTM. However, THF slowly elutes a third component, now believed to be an adsorbed ionic tin-containing compound.

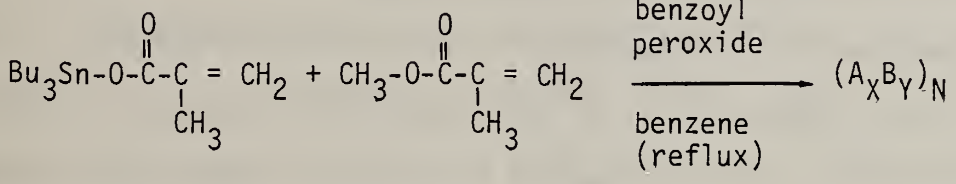
We now verify that a one percent solution of acetic acid (HOAc), injected into the THF mobile phase after a measured delay, efficiently desorbs the third species, without hydrolyzing polymeric TBT-substituted esters.

Tin-selective SEC-GFAA of a series of partially reacted OMPs indicates that the TBT-substituted esters partially decompose during one year of storage at -78 °C, but mass sensitive SEC-ΔRI indicates that the polymer backbone remains intact. Comparison of SEC-GFAA and SEC-ΔRI suggests a convenient chromatographic method for determining reaction kinetics of both MMA and TBTM simultaneously.

Keywords: Acetic acid, adsorption, differential refractive index. fractionation, graphite furnace atomic absorption, kinetics, methyl methacrylate, organometallic copolymer, SEC, stability, tributyltin acetate, tributyltin methacrylate.

1. INTRODUCTION

A class of experimental biocidal slow release triorganotin compounds is prepared by the free radical initiated copolymerization of two or more monomeric species.[1,2] The synthesis of an extensively tested organometallic polymer (OMP) is depicted in Equation 1:



$$Bu_3Sn\text{-}O\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}\underset{CH_3}{\underset{|}{C}} = CH_2 + CH_3\text{-}O\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}\underset{CH_3}{\underset{|}{C}} = CH_2 \xrightarrow[\text{benzene (reflux)}]{\text{benzoyl peroxide}} (A_X B_Y)_N \qquad (1)$$

(A) (B)

The starting materials for this copolymer (OMP-2) are tributyltin esters of methacrylic acid (A = TBTM) and methyl methacrylate (B = MMA). The end product includes not only a high polymer tin-bearing species, but also a species of low MW (TBTM), well resolved in the size exclusion chromatogram obtained on μStyragel, and a third component that is retained by an adsorption rather than a size exclusion mode. Thus, the product is a formulation or mixture rather than a single polymeric species. This situation is typical of many commercial OMP's tested in our laboratory.[3] OMPs are very toxic substances; coated on exposed marine surfaces, they confer long-term protection against fouling by microorganisms.[4] Initial rapid leaching of tin-bearing species is followed by a zero-order rate of release that continues for several years. Consequently, it is of great interest to the U.S. Navy to fully specify their performance in terms of polymer design, but the protective mechanism is complex.

An urgent need is to characterize the controlled-release mechanism or mechanisms. What processes are involved in protection and leaching? What environmental problems might arise from extensive use of OMPs at sea? To answer these questions and to provide background information for a Military Specification, the National Bureau of Standards has developed novel chromatographic methods of molecular characterization for OMPs, based on determination of the distribution of tin in the polymer.

In collaboration with the David Taylor Naval Ship Research and Development Center, Annapolis, MD, we have applied these methods for the rapid determination of various parameters of molecular composition: weight average molecular weight (Mw), number average molecular weight (Mn), molecular weight distribution (MWD), monomer conversion, and reaction kinetics, all based on the distribution of tin in separated polymer fractions.[3, 5-7]

This report summarizes research undertaken during FY82:

- The size exclusion chromatogram of a typical OMP (OMP-2)
- The ability to force abrupt truncation of tailing by delayed injection of discrete amounts of dilute acetic acid
- Evidence for the partial decomposition of polymer esters on storage at -78 °C
- The feasibility of dual methods of detection to aid in the kinetic analysis of the copolymerization.

This work was presented as a poster session at the VI International Symposium on Column Liquid Chromatography, Cherry Hill, New Jersey, June 6-11, 1982, and has been accepted for publication in the Journal of Chromatography. It concerns characterization by SEC only. Recommendations for additional research are discussed.

Characterization of OMPs by FT-NMR, with supporting SEC-GFAA will be the subject of a forthcoming report.

2. EXPERIMENTAL

2.1 Apparatus and Chemicals*

In figure 1 is given a block diagram of the chromatographic analysis system used. Solutions are injected into flowing eluents at the sample injection port. Analytes separated on the column are detected by one or more of: ultraviolet absorption, differential refractive index, or element specific GFAA. The apparatus used has been described in detail.[3, 5-7] All chemicals used were reagent grade. The mobile phase in all of the experiments reported herein consisted of tetrahydrofuran (THF) with and without addition of pyridine or acetic acid (HOAc).

2.2 Preparation of Copolymer

The OMP-2 copolymer (figure 2) was prepared by the reaction of TBTM and MMA in 1:1 molar proportions by refluxing in reagent grade benzene (monomer to solvent ratio 1:2 w:v) as described by Dyckman and Montemarano.[1] The TBTM was prepared from highly purified tributyltin oxide and methacrylic acid.[8] MMA was commercially prepared, inhibited with 25 ppm of hydroquinone, and used as received.

This OMP exhibits the following properties:

- A clear viscous liquid
- Soluble in organic solvents
- Very toxic to humans as well as microorganisms
- A mixture of MW fractions

---

*Certain commercial materials and equipment are identified in this paper in order to specify the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

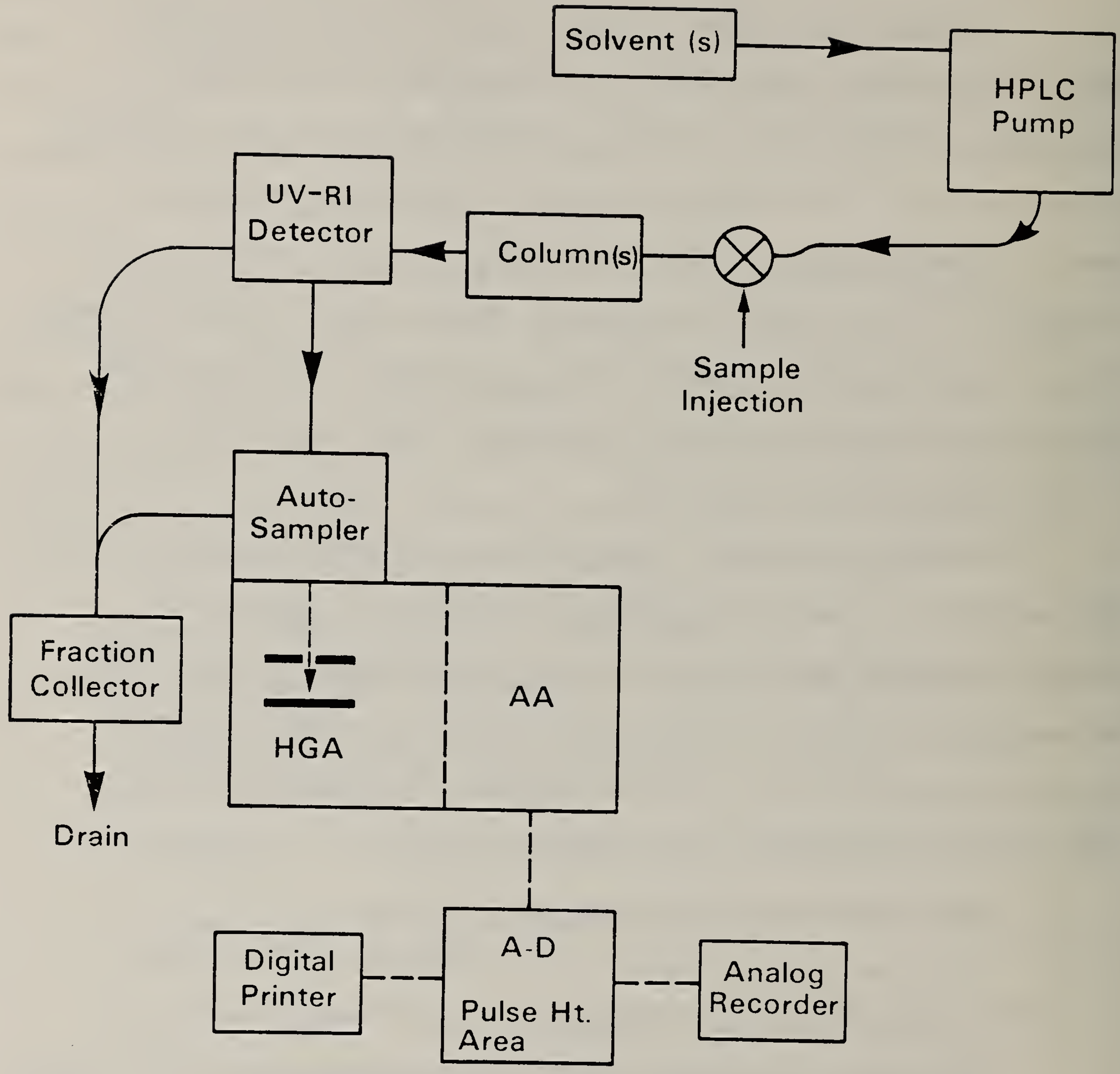
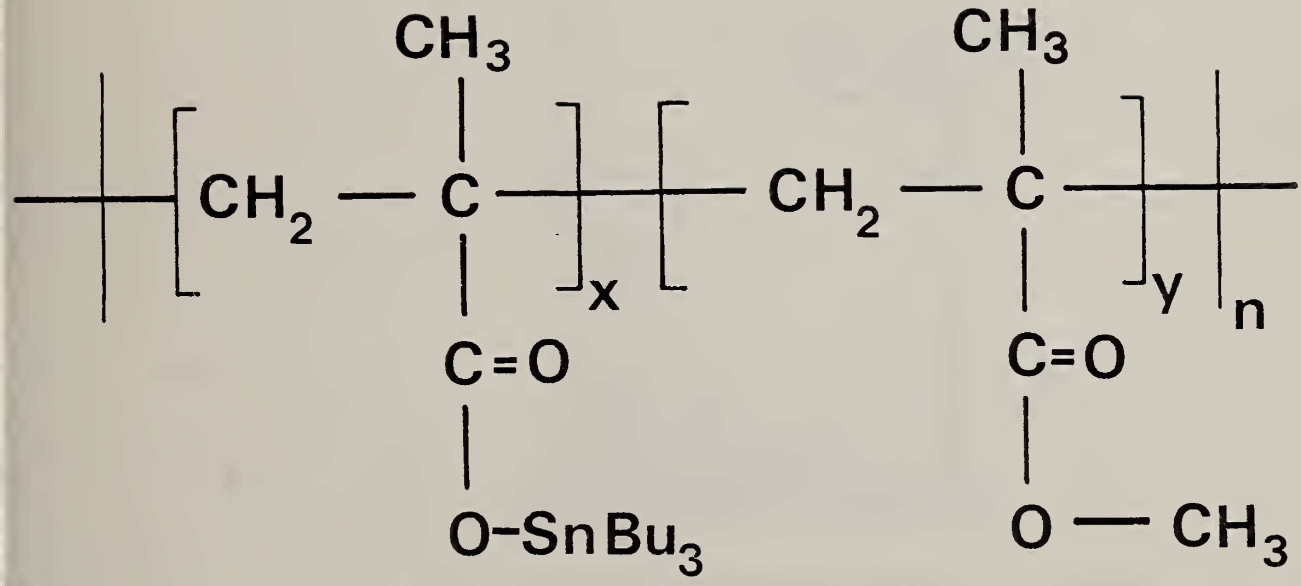


Figure 1. Block diagram summarizing the SEC-UV/ΔRI-GFAA system, including accessory devices. The GFAA spectrophotometer consists of a heated graphite atomizer (HGA) and an atomic absorption spectrophotometer (AA). In the present work, either the auto-sampler continuously transferred 20 μL eluent specimens into the graphite furnace at present 45-60 sec intervals, or batch fractions were collected during elution for subsequent quantitation of tin.



$$\left[\left[\mathrm{CH_2} - \overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \underset{\displaystyle \mathrm{O{-}SnBu_3}}{\mathrm{C{=}O}}}{\mathrm{C}}} \right]_x \left[\mathrm{CH_2} - \overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \underset{\displaystyle \mathrm{O{-}CH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}} \right]_y \right]_n$$

Figure 2. The suggested formula of a copolymer prepared by the free-radical addition of TBTM to MMA. The subscripts x and y represent numbers of monomers and n represent numbers of repeat units. Neither the numbers x, y, or n, nor the tacticity of the copolymer is assumed to be constant.

3. RESULTS AND DISCUSSION

3.1 Chromatograms of OMP-2 (figure 3) and TBTM (figure 4).

Chromatograms of the type depicted in figure 3 yield much useful information. The scope is indicated in the following paragraphs.

3.1.1 Apparent Molecular Weights

1. The apparent MW of individual chromatographic peaks is based on calibration with polystyrene MW standards.[3]

2. The weight average (M_w) and number average M_n molecular weights are given by equations (2) and (3)

$$M_w = \frac{\sum_{i=1}^{n} h_i M_i}{\sum_{i=1}^{n} h_i} \tag{2}$$

$$M_n = \frac{\sum_{i=1}^{n} h_i}{\sum_{i=1}^{n} h_i / M_i} \tag{3}$$

In these equations h_i is the observed height of the ith peak whose molecular weight is M_i.

3.1.2 Molecular Weight Distribution

The complete molecular weight distribution (MWD) can only be given by a plot of relative concentrations versus molecular weight. Nevertheless, a useful shorthand expression defines MWD as M_w/M_n. Defined thus, MWD is exactly 1.0 only for a perfectly homogeneous polymer. For any real polymer, MWD > 1.0; the magnitude of MWD correlates approximately with the width of the polymer peak (range of molecular weights) in SEC.

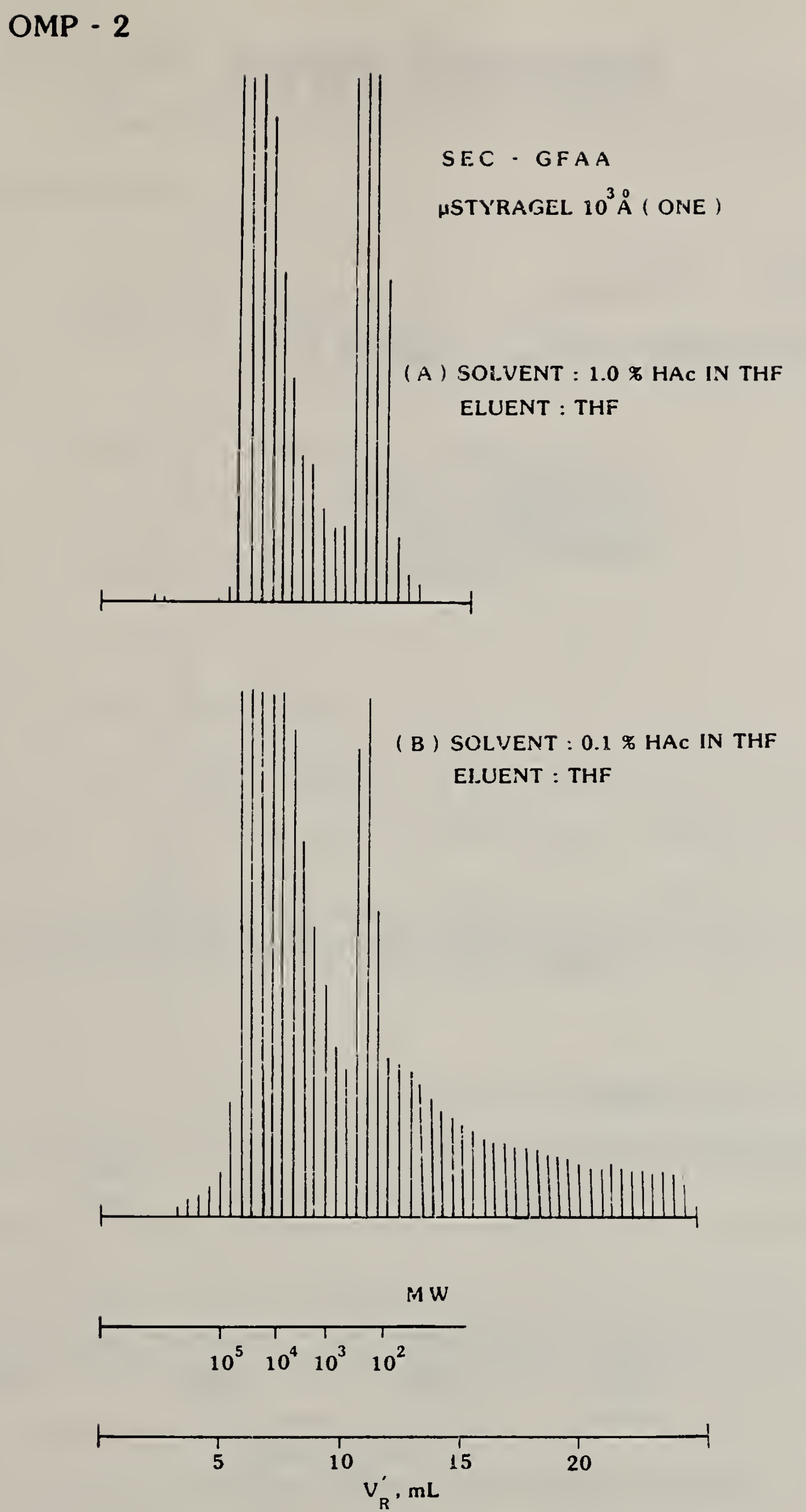


Figure 3. SEC-GFAA chromatogram of OMP-2. Solvent, THF. Column, μStyragel (one), average pore size 10^3 Å. Mobile phase, THF. Flow rate 0.5 mL min^{-1}. SEC detector, Perkin-Elmer 360, equipped with an Sn-specific EDL lamp operating at 224.6 nm. Injected volume 50 μL. Injected concentration 50 μg/50 μL.

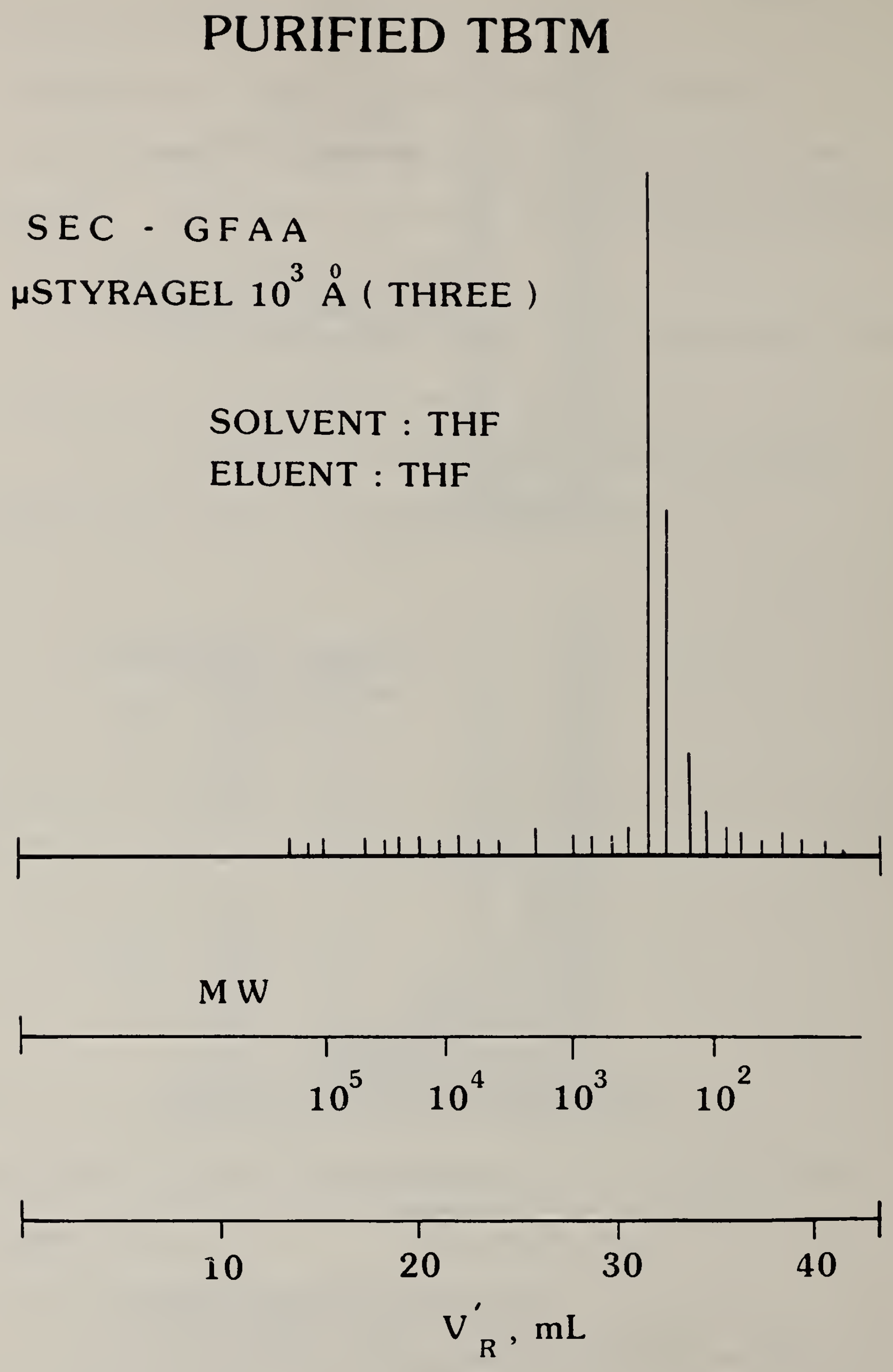


Figure 4. SEC-GFAA chromatogram of TBTM purified by recrystallization from petroleum ether. Solvent, THF. Mobile phase, THF. Columns, μStyragel (three) in series; average pore size 10^3 Å. Flow rate 1.0 mL min^{-1}, SEC detector, Perkin-Elmer 360. Injected volume, 50 μL. Injected concentration of TBTM, 50 μg/50 μL.

3.1.3 Extent of Polymerization

The extent of conversion of TBTM to copolymer is obtained by equation (4)

$$\Delta P(\%) = \Delta \left(\frac{A}{A+B}\right) \times 100 \qquad (4)$$

where A = polymer (OMP) peak area

B = monomer (TBTM) peak area

$\Delta P(\%)$ = percent conversion

3.1.4 Polymerization Rates

ΔP is a linear function of the logarithm of the reaction time, as we shall see. From such data, polymerization reaction rates have been determined chromatographically.[6] Obviously, kinetic analysis requires accurate measurement of the variables A and B.

3.1.5 Impurities in OMP-2

The quantitation of unreacted TBTM in SEC-GFAA chromatograms is complicated by extensive tailing such as that typically observed (figure 3). However, figure 4 demonstrates that TBTM is reproducibly eluted with a narrow V_R. Thus we conclude that tailing in figure 3, is not due to adsorbed TBTM but to new tin-containing impurity species.

To quantitate TBTM, i.e., the value of B, from chromatograms, it is necessary to summarize only those peak heights corresponding to molecular species of MW 100-500 daltons.

Partially retained or tailing species are eluted by a mechanism other than size exclusion. This implies that the species retained is of different polarity from neutral TBTM. Its desorption will be critical for the complete characterization of OMP-2 in support of the Navy Mil-Spec.

3.2 Desorption of Tailing Organotin Species

In the course of systematic attempts to desorb the tailing component of OMP-2, we found that a strongly basic mobile phase containing an electron-donor [5 percent (v:v) pyridine in THF] was not more effective than the less basic solvent THF alone.

On the other hand, desorption is effected by glacial acetic acid (HOAc) in THF, as demonstrated by the abrupt termination of tailing shown in figure 5. To obtain these data, injection of the polymer solution was followed, after a measured period of time, by injection of a trace amount of HOAc (1.0 percent in THF, 50 μL). The late-appearing spike follows elution of TBTM by a period of time (or elution volume, V_R) corresponding to the delay between injections.

These data indicate that HOAc reacts in some manner with the μStyragel-bound species, resulting in desorption of another tin-bearing species not subject to adsorption. The release reaction is apparently not stoichiometric. Figure 6 illustrates that:

(1) When the polymer solution (1.0 percent w:v) contains 1.0 percent (v:v) glacial acetic acid, the acid is necessarily coinjected with the polymer. No tailing occurs, but a large low MW peak bearing the same retention volume as TBTM results.

(2) If the acetic acid concentration is only 0.1 percent (v:v) and the OMP concentration is 1.0 percent (w:v), the reduced amount of acid is insufficient to overcome tailing. There is, nonetheless, a substantial enhancement of the low MW peak.

From these results, we conclude that a competitive mechanism involving acidic ion-exchange sites on μStyragel is involved, causing a shift in retention pattern.

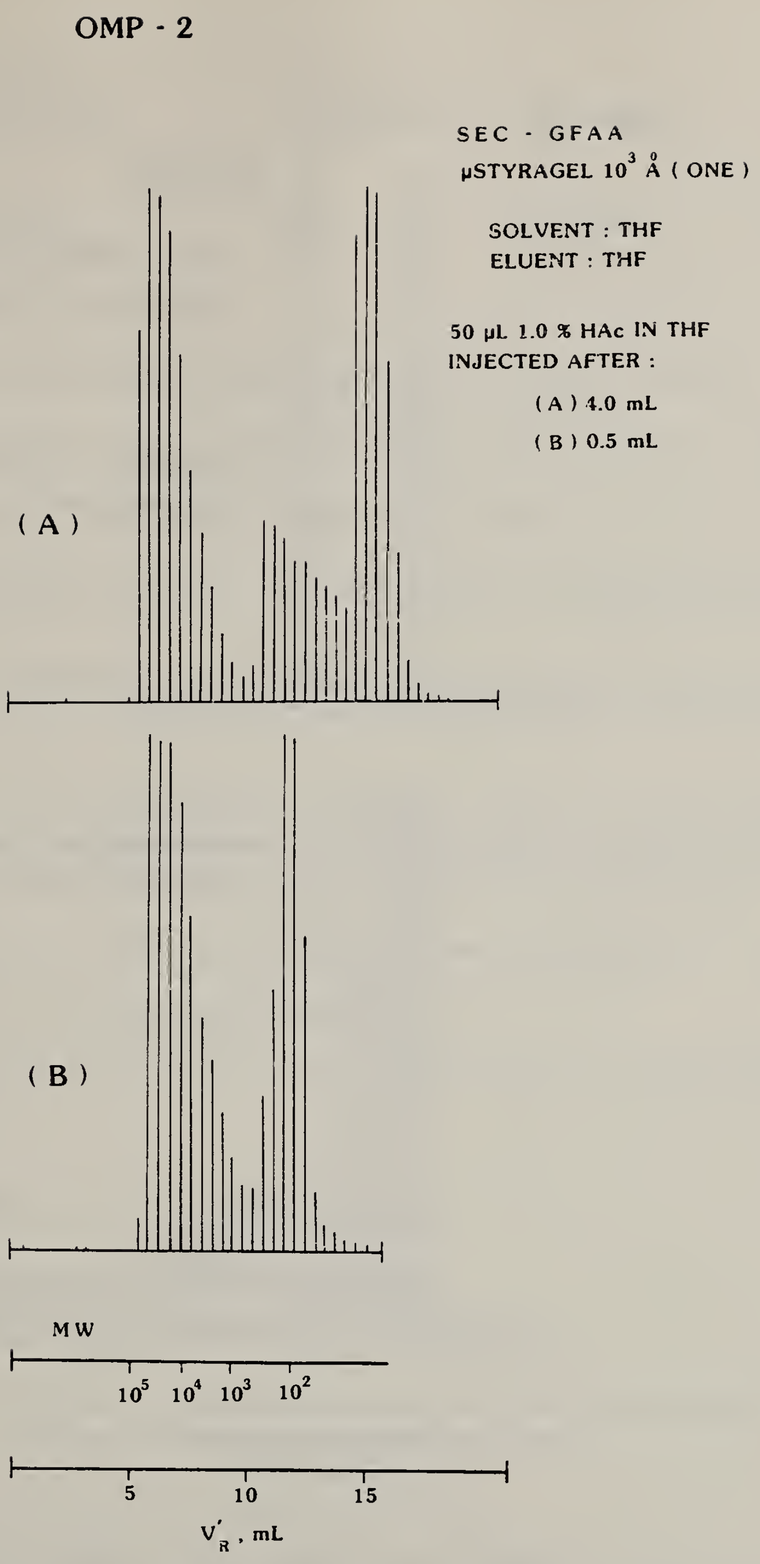


Figure 5. SEC-GFAA chromatograms of OMP-2.
(A) Solvent THF. Mobile phase, THF. 50 μL of THF containing 1.0 percent HOAc (v:v) introduced into the THF mobile phase 8.0 min (4.0 mL) after injection of the OMP solution. All other conditions the same as for figure 3.
(B) All conditions the same as (A), except that 50 μL of 1.0 percent HOAc in THF was introduced 1 min (0.5 mL) after the solution of OMP-2.

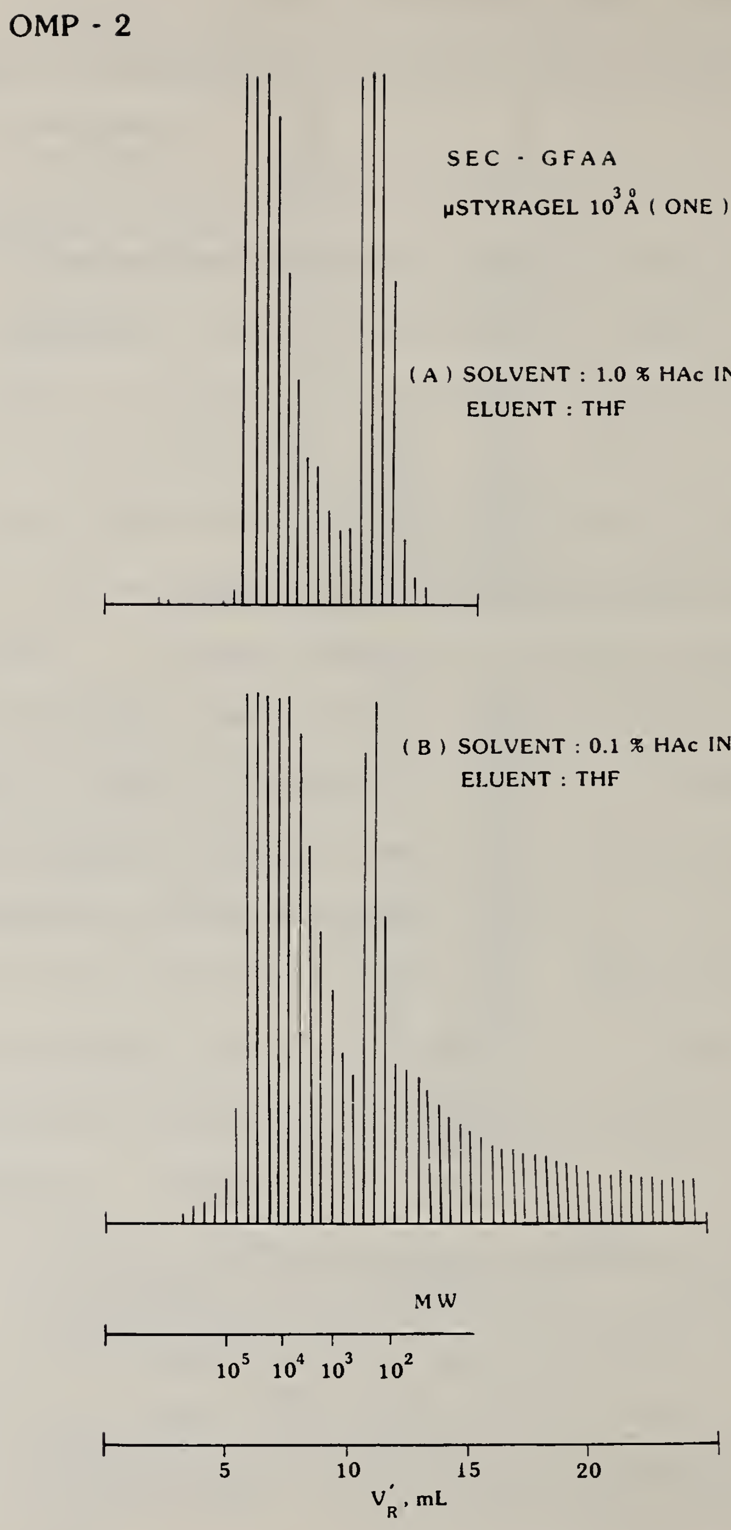
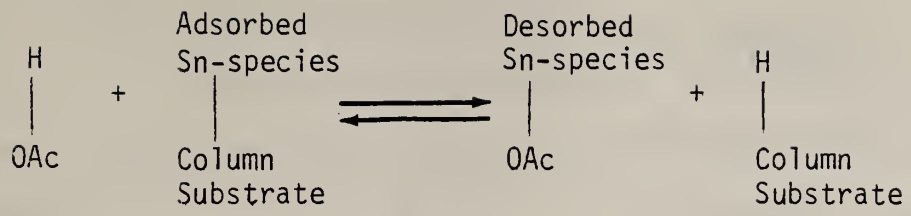


Figure 6. SEC-GFAA chromatograms of OMP-2.
(A) Solvent, THF containing 1.0 percent HOAc; acid added 1.0 h prior to injection. All other conditions same as for figure 3.
(B) Solvent, THF containing 0.1 percent HOAc, acid added 1.5 h prior to injection. All other conditions same as for figure 3.



$$\begin{array}{c}\mathrm{H}\\ | \\ \mathrm{OAc}\end{array} + \begin{array}{c}\text{Adsorbed}\\ \text{Sn-species}\\ | \\ \text{Column}\\ \text{Substrate}\end{array} \rightleftharpoons \begin{array}{c}\text{Desorbed}\\ \text{Sn-species}\\ | \\ \mathrm{OAc}\end{array} + \begin{array}{c}\mathrm{H}\\ | \\ \text{Column}\\ \text{Substrate}\end{array} \qquad (5)$$

Comparison of the chromatogram depicted in figures 3 and 5 suggest that acetic acid also hydrolyses the OMP-2 polymer itself. This conclusion was verified by experiments typified by figure 7.

(1) The low MW SEC-GFAA peak is much greater in area than the high MW peak.

(2) These proportions are consistent with acid hydrolysis of polymer esters, and co-elution with TBTM, of a derivatized species.

(3) Tailing in the chromatogram probably is due to continuing hydrolysis of the polymer as it is eluted by the THF/1.0% HOAc solution, with continuing elution of a derivative.

Therefore it is necessary to avoid coinjecting polymer and acids.

3.2.1 Nature of the Desorption Mechanism

A number of questions are suggested by the chromatograms presented in figures 3-7:

(A) What is the adsorbed species?

(B) What is the desorbed species?

(C) What is the mechanism of desorption?

1. Competition between acid and adsorbed species?
2. On-column derivatization?

Several clues have been noted above:

(1) When HOAc is added at the same time as the dissolved polymer, the desorbed species co-elutes with TBTM.

(2) This suggests that the desorbed species and TBTM are of the same polarity.

(3) In turn, the on-column change in polarity suggests on-column derivatization.

(4) This, in turn, suggests that a cation such as tributyltin cation (TBT^+)[9] is the adsorbed species.

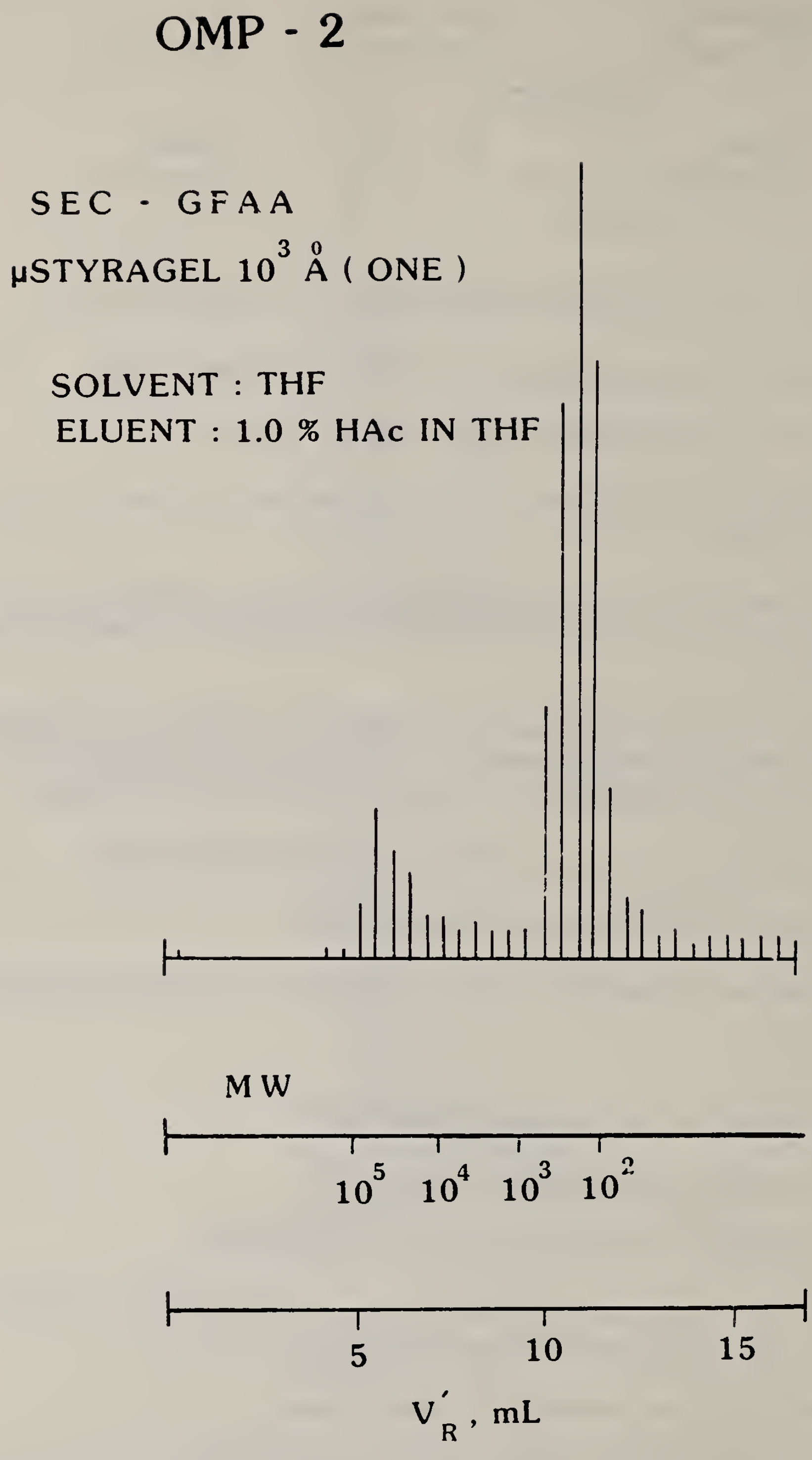


Figure 7. SEC-GFAA chromatogram of OMP-2 undergoing acid hydrolysis. Mobile phase, THF containing 1.0 percent HOAc. All other conditions the same as for figure 3.

3.2.2 Future Studies Required

Since conclusive evidence for any definite species is lacking, future research will include the following chromatographic experiments:

(1) Spiking OMP-2 with TBTOAc and/or other species prior to chromatography.

(2) Running TBTOAc with and without HOAc.

(3) Substituting an injected mineral acid for HOAc.

(4) Combining SEC and strong cation exchange chromatography (SCX) to isolate cationic species.

3.3 Kinetic Investigation of OMP-2 Copolymerization Combining SEC-GFAA and SEC-ΔRI

3.3.1 SEC-GFAA of Partially Reacted Samples

The definition of ΔP, the degree of polymerization is given in equation (4), section 3.1.3. We have reported[6] that the copolymerization of MMA and TBTM under free radical conditions exhibits a high linear correlation with the logarithm of the time of reaction.

$$\Delta P = k\Delta \ln t + b \tag{6}$$

where k and b are constants, and t is the time of reaction in minutes.

The published experiment was repeated on a second series of partially reacted samples. The result shown in figure 8 (closed circles) shows that the experiment is reproducible in spite of the extent of tailing in individual chromatograms, e.g., the two chromatograms shown in figure 9 are included in the slope having $k = 7.85$ and $r = 0.985$, where "r" is the coefficient of linear correlation.

Because data collection on these samples was not continued to the complete extinction of tailing, we decided to reexamine them

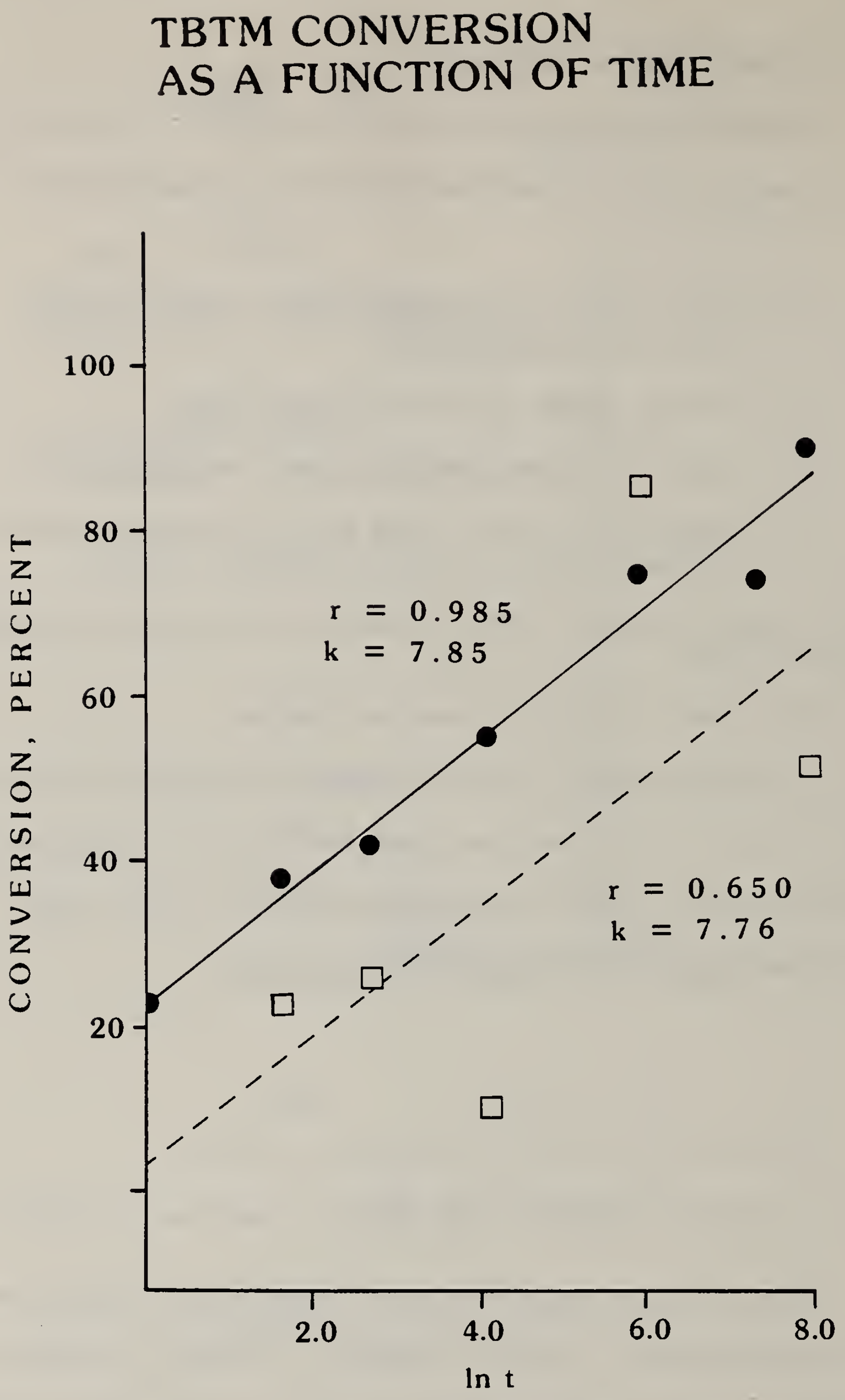


Figure 8. Polymerization rate (k) of TBTM. Closed Circles. Conversion of TBTM during the copolymerization of TBTM and MMA, determined shortly after the samples were synthesized. Data taken from chromatograms including those depicted in figure 9.

Open squares. Conversion of TBTM, as calculated from data obtained after one year of storage at -78 °C, and including the chromatograms depicted in figure 10.

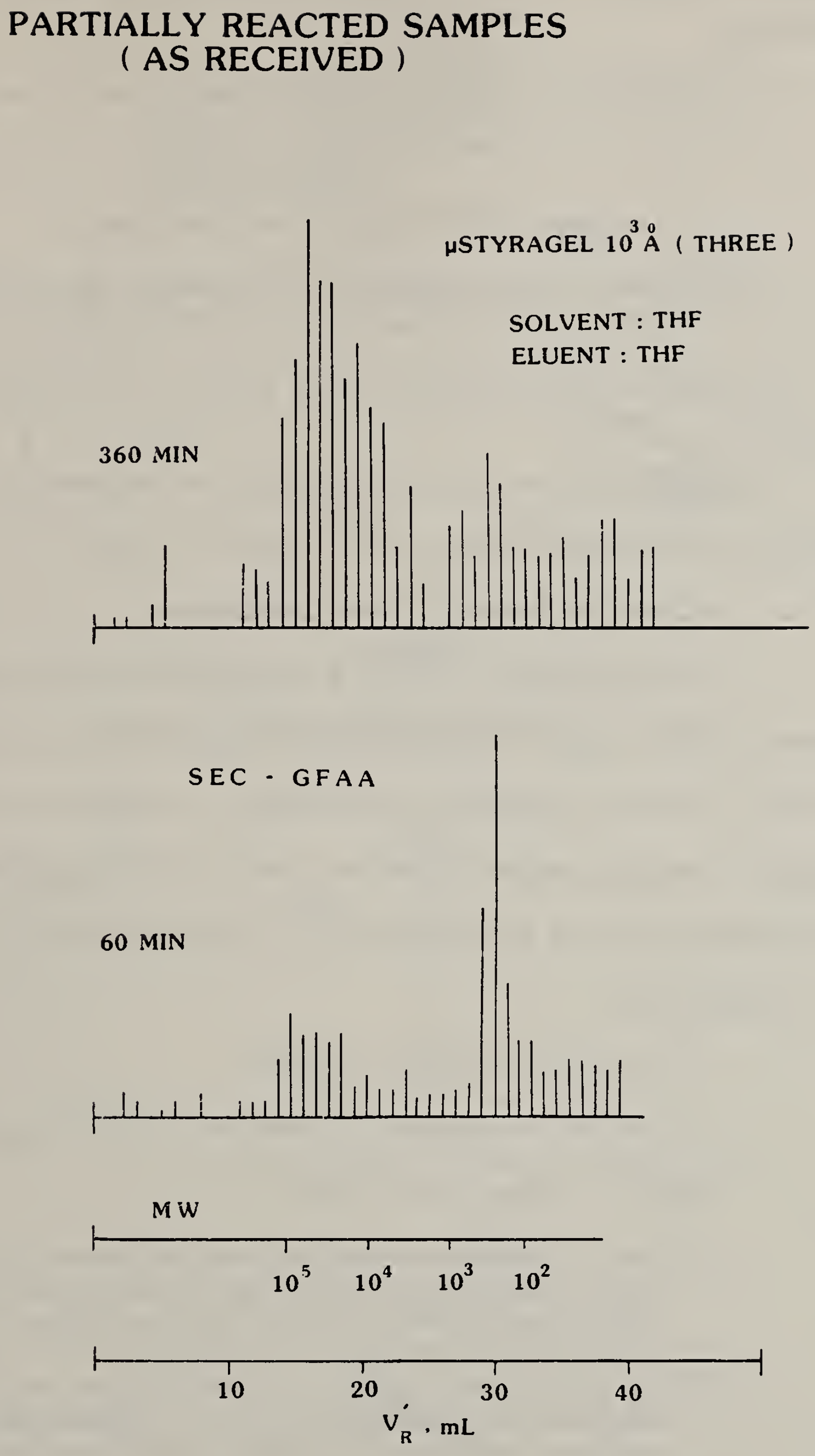


Figure 9. SEC-GFAA chromatograms of partially reacted specimens during the copolymerization of TBTM and MMA. Solvent, THF. Mobile phase, THF. Flow rate 1.0 mL min^{-1}. Columns, μStyragel (three), average pore size 10^3 Å. All other conditions same as for figure 3.

after one year of storage at -78 °C, using desorption by HOAc with delayed injection.

The results (figure 8, open square, and figure 10) show that:

(1) The good fit of points has been lost.

(2) Very large quantities of desorbed species are present in the samples reacted either 60 or 360 minutes.

(3) Much more desorption is evident in the 360 minute sample.

These data are consistent with the decomposition of polymer esters on prolonged storage in THF, even at -78°.

3.3.2 SEC-ΔRI of Partially Reacted Samples

SEC-ΔRI involves use of a mass-sensitive detector. Hence, conversion plots result from addition of both TBTM and MMA as a function of time, unlike tin-specific SEC-GFAA. Our objective in obtaining SEC-ΔRI characterizations was to determine the difference between the rates of TBTM conversion and mass conversion, and from this difference ultimately to determine:

(1) the rate of MMA conversion

(2) the relative rates of MMA and TBTM conversion.

Figure 11 demonstrates that:

(1) Mass conversion exhibits a high linear coefficient of correlation with the log of reaction time, at least for the first 80-85 percent conversion.

(2) This high coefficient of correlation persists after one year of storage at -78 °C, suggesting that the polymer backbone is stable under these conditions.

(3) The rate of conversion appears to slow down between 85 percent and 90 percent conversion, possibly showing concentration effects.

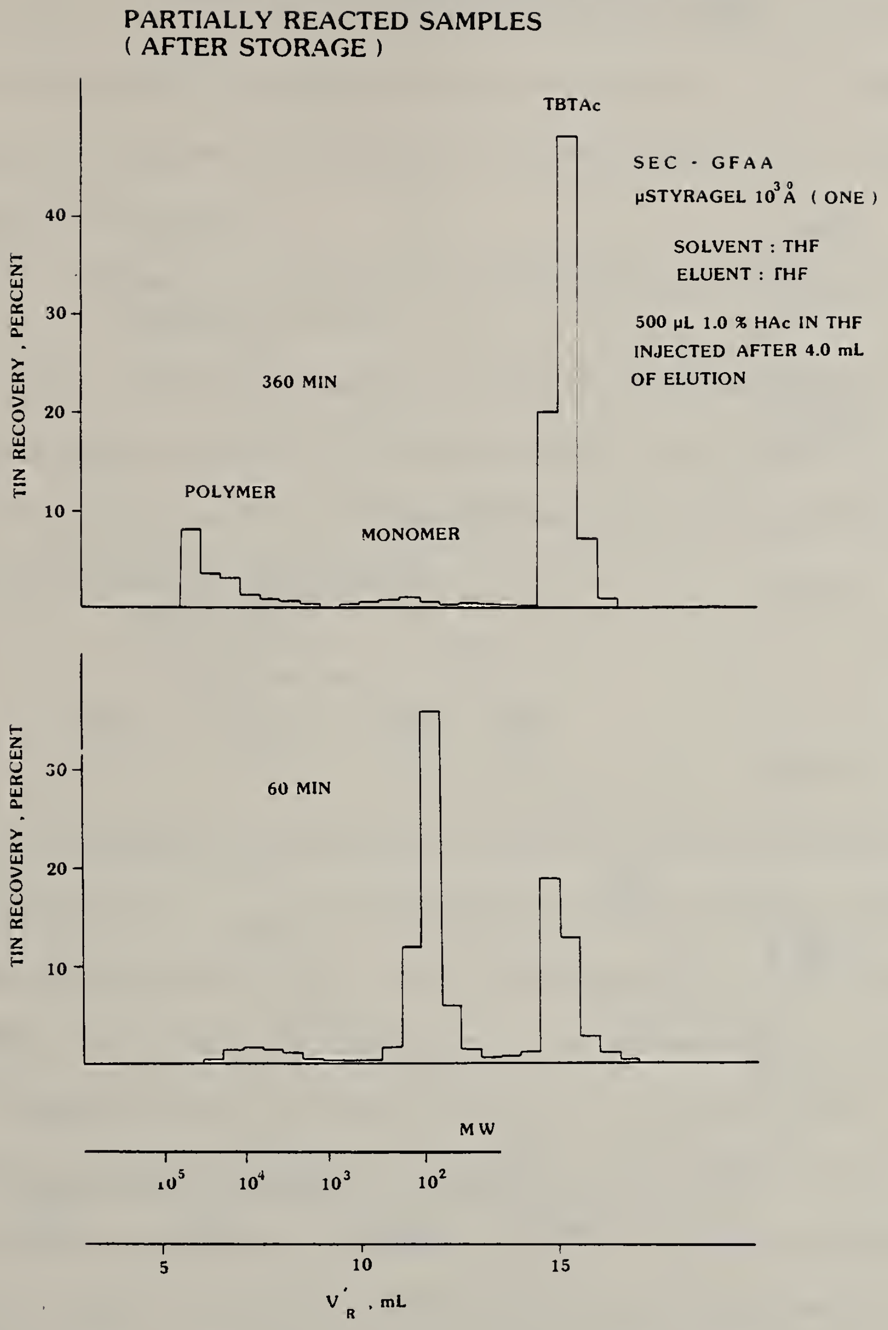


Figure 10. Partially reacted specimens retested after one year of storage at -78 °C. Histogrammic peak height indicates tin content of fractions. Solvent, THF. Mobile phase, THF. Flow rate 0.5 mL min^{-1}. Column, μStyragel (one), pore size 10^3 A. Injected volume, 500 μL. Injected concentration 100 μg/500 μL. 500 μL of 1.0 percent HAc in THF introduced by injection 8 min (4.0 mL) after the injection of polymer.

MASS CONVERSION AS A FUNCTION OF TIME

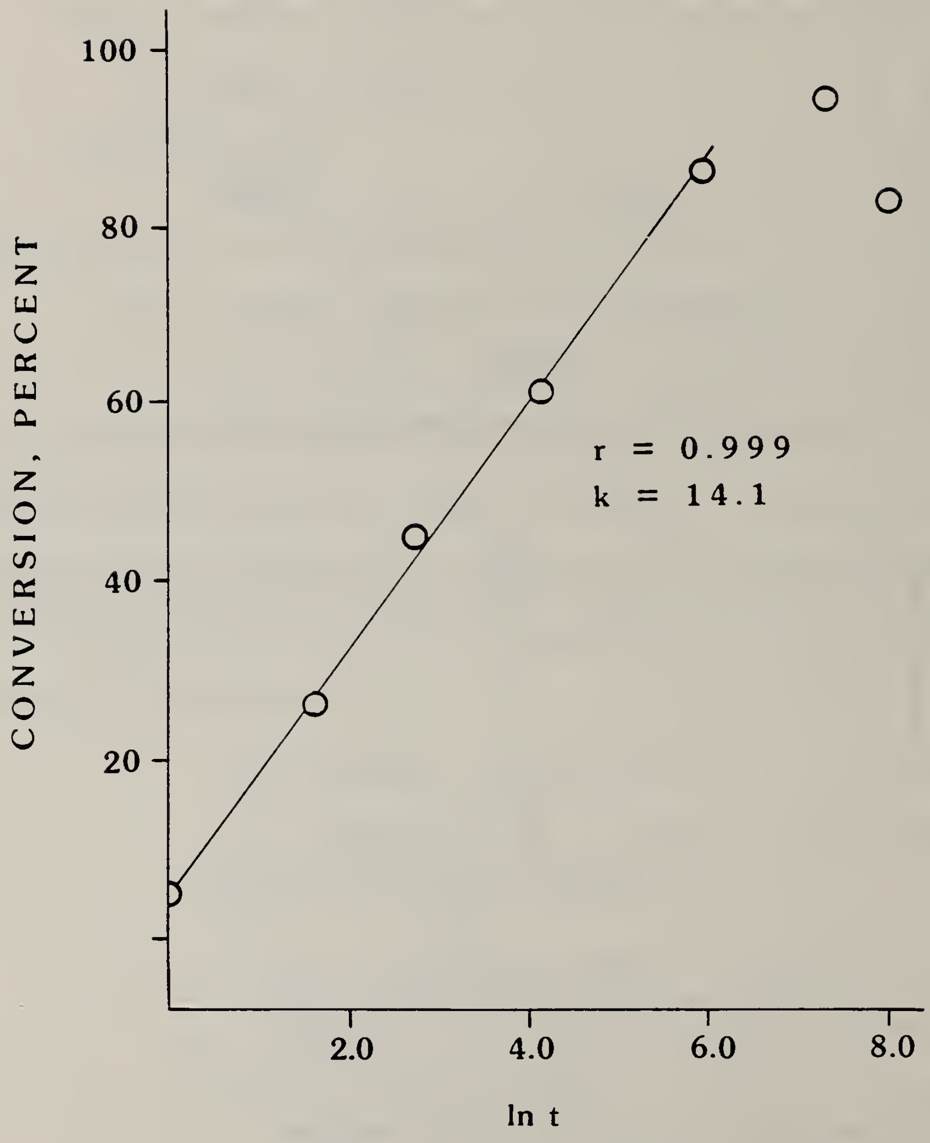


Figure 11. Mass conversion of low-MW to high-MW materials during the copolymerization of TBTM and MMA, plotted as a function of the reaction time. Conversion data were calculated from chromatograms including those in figure 9.

(4) The final point is bad for unknown reasons.

(5) The rate of mass conversion is approximately 1.8 times greater than the rate of TBTM conversion.

Typical chromatograms from which these data were obtained are illustrated in figure 12. The enclosed darkened areas determined by planimetry were used in the calculations of conversion. The "negative" peaks are due to benzene and, probably, preservatives (e.g., hydroquinone, hydroxylated butyltoluene).

3.3.3 Comparative Utility of Combination of GFAA and ΔRI Detectors for SEC.

The data presented in figures 8-12 are especially interesting because they point the way to a novel and convenient method of discovering the proportions of two monomers in an organometallic polymer from the derived equation:

$$K_{MMA} = \sigma(K_{MASS} - K_{TBTM}) \tag{7}$$

Here K_{MMA} is a parameter governing the rate of addition of MMA (on a mass basis) to the growing chain. K_{MMA} is proportional to the difference between the rate of increase in total mass (K_{MASS}) and in TBTM(K_{TBTM}). If MMA and TBTM contribute equally to observed differences in refractive index, then K_{MMA} is estimated immediately and the ratio of K_{MMA} to K_{TBTM} gives their relative concentrations in the copolymers. To convert from a mass to a molecule basis is simple given the molecular weights: TBTM = 375 daltons, and MMA = 100 daltons. The essential step is to determine the relative contributions of TBTM and MMA to the refractive index of a mixture of both substances.

Since the relative rates of conversion depend on the relative reactivities of the monomers under actual conditions, the composition of the growing chain would be predictable by equation (4).

This will be useful in engineering the synthesis of OMP's, since measurement of relative reactivities is both difficult and time consuming by alternative methods.

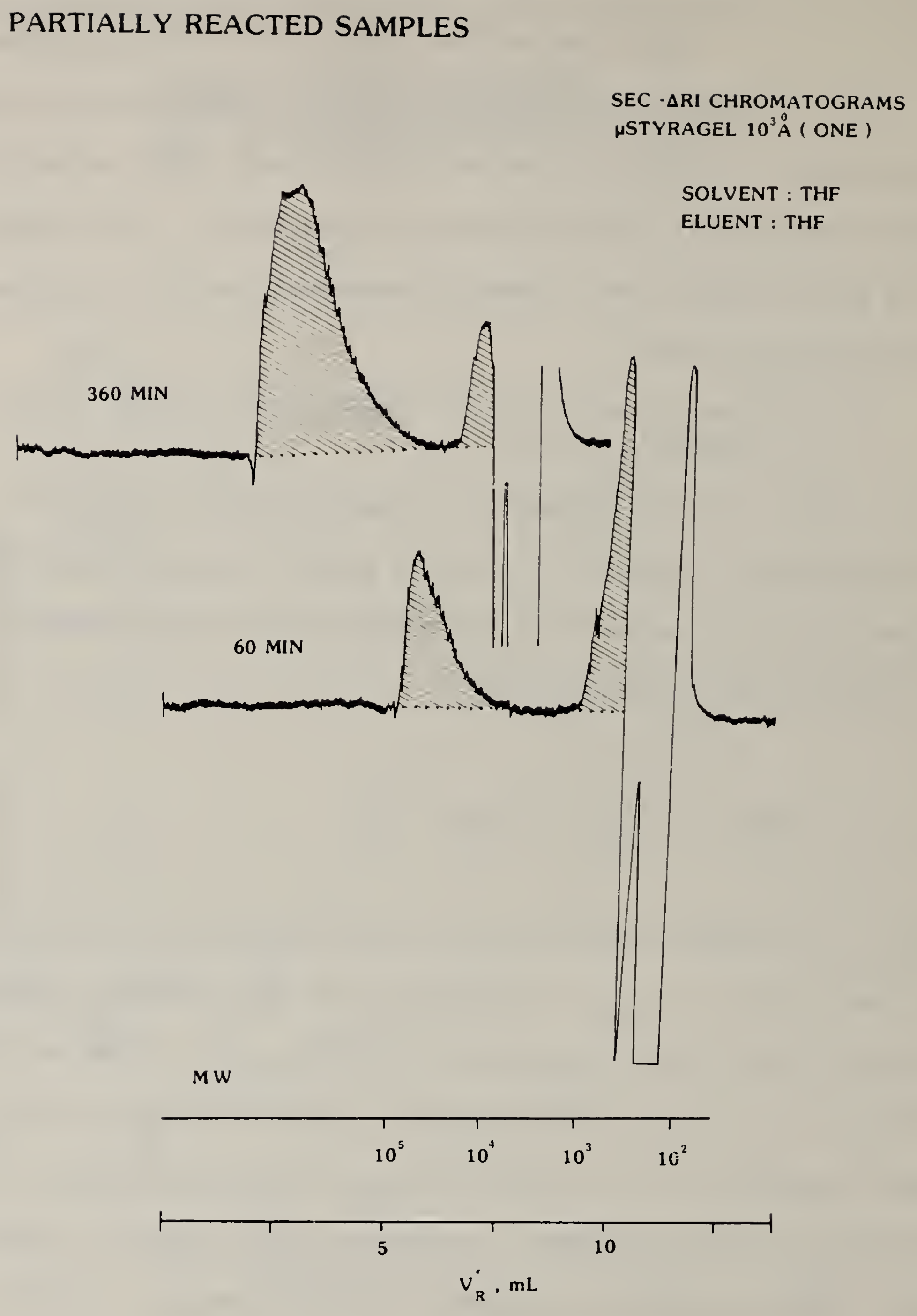


Figure 12. SEC-ΔRI chromatograms of samples taken during the copolymerization of TBTM and MMA and stored one year at -78 °C. Solvent, flow rate, mobile phase and column the same as for figure 10. Detector, Knauer dual detector; ΔRI sensitivity, 6×10^{-8} ΔRI unit = full scale deflection. Injected volume 500 μL. Injected concentration 1000 μg/500 μL. Note offset of upper chromatogram to avoid overlap.

However, it is still necessary to determine the reproducibility of the mass- and TBTM conversion constants, and the relative weights of TBTM and MMA in the ΔRI measurements before the method can be fully implemented.

4. CONCLUSIONS

The research described in this report was designed to provide basic information of the type necessary for writing a Mil-Spec for organometallic polymers and their synthesis. This work considerably broadens the scope of the analytical SEC-UV/ΔRI-GFAA reported in our earlier papers.

4.1 It is now possible to terminate tailing in SEC-GFAA chromatograms.

4.1.1 Thus, it is shown that OMP-2 mixtures include a species, probably a cation of low MW, that is adsorbed in substantial quantity on μStyragel.

4.1.2 Decomposition at -78 °C occurs, involving the pendant TBT-esters but probably not the polymer backbone.

4.1.3 The combination of SEC-GFAA and SEC-ΔRI, in line or in tandem, holds great promise as an analytical and engineering aid in the design of OMPs.

4.2 Future research must be designed to:

4.2.1 Identify the adsorbed species;

4.2.2 Characterize the measured rate of mass conversion in terms of the transport of MMA as well as TBTM, on a molecular basis;

4.2.3 Verify the reproducibility of results determined in 4.2.1 and 4.2.2 by carrying out model synthesis with kinetic analysis by SEC-UV/ΔRI-GFAA.

5. ACKNOWLEDGMENTS

The work described in this report was partially supported by the David Taylor Naval Ship Research and Development Center (DTNSRDC, Annapolis, MD) to whom we extend our thanks. For valued discussion and suggestions, we are indebted to C. S. Weiss, D. W. Brown and W. R. Blair, all of NBS; and to V. J. Castelli, C. E. Mullen, and D. M. Andersen, all of the DTNSRDC (Annapolis).

6. REFERENCES

[1] Dyckman, E. J.; Montemarano, J. A. Antifouling Organometallic Polymers: Environmentally Compatible Materials, Naval Ship R&D Center, Bethesda, MD., Report No. 4186, 1974. 31 p.

[2] Yeager, W. L.; Castelli, V. J. Antifouling Applications of Various Tin-Containing Organometallic Polymers, in Organometallic Polymers, C. E. Carrahar, Jr., J. E. Sheats, and C. U. Pittman, Jr., Eds., Academic Press, NY, 1978, pp. 175-180.

[3] Parks, E. J.; Brinckman, F. E. Characterization of bioactive organotin polymers: fractionation and determination of MW by SEC-GFAA, in Controlled Release of Pesticides and and Pharmaceuticals, D. H. Lewis, Ed., Plenum Press, NY, 1981, pp. 219-238.

[4] Castelli, V. J.; Becka, A. M. Status Report on OMP Materials, David W. Taylor Research and Development Center DTNSRDC SME 82-39, Bethesda, MD, 20084; May 1982.

[5] Parks, E.J.; Brinckman, F. E.; Blair, W. R. Application of a graphite furnace atomic absorption detector automatically coupled to a high performance liquid chromatograph for speciation of metal-containing macromolecules. J. Chromatogr. 185, 563; 1979.

[6] Parks, E. J.; Brinckman, F. E.; Mullin, C. E.; Andersen, D. M.; and Castelli, V. J. Characterization by tin-specific size exclusion chromatography of the free radical copolymerization of tributyltin methacrylate and methyl methacrylate. J. Appl. Poly. Sci. 26, 2967; 1981.

[7] Parks, E. J.; Johnannesen, R. B.; Brinckman, F. E. Characterization of Organometallic Polymers by Chromatographic Methods and Nuclear Magnetic Resonance, Nat. Bur. Stand. (US) NBSIR81-2424; December, 1981. 35 p.

[8] Montermoso, J. C.; Andrews, T. M.; Marinelli, L.P. Polymers of tributyltin acrylate esters. J. Poly. Sci. 32, 523; 1958.

[9] Jewett, K. L.; Brinckman, F. E. Speciation of trace di- and triorganotins in water by ion exchange HPLC-GFAA. J. Chromatogr. Sci. 19, 583; 1981.

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 82-2577	2. Performing Organ. Report No.	3. Publication Date September 1982

4. TITLE AND SUBTITLE

ADVANCES IN THE SEC CHARACTERIZATION OF ORGANOMETALLIC COPOLYMERS AND COPOLYMERIZATION: DESORPTION OF CHARGED SPECIES BY INJECTED DILUTE ACETIC ACID

5. AUTHOR(S)

E. J. Parks, R. B. Johannesen, and F. E. Brinckman

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The chemical characterization of controlled-release, biocidal triorganotin-containing copolymers (organometallic polymers, OMPs) is necessary for predicting the in-service performance of these important materials. An OMP investigated in the present research was prepared by the free radical copolymerization of tributyltin methacrylate (TBTM) and methylmethacrylate (MMA). Size exclusion chromatography (SEC) on μStyragel, coupled with an in-line graphite furnace atomic absorption detector (GFAA) quantitates the bioactive tin in at least two well-resolved fractions: a polymer fraction, and, probably, unreacted TBTM. However, THF slowly elutes a third component, now believed to be an adsorbed ionic tin-containing compound.

We now verify that a one percent solution of acetic acid (HOAc), injected into the THF mobile phase after a measured delay, efficiently desorbs the third species, without hydrolyzing polymeric TBT-substituted esters.

Tin-selective SEC-GFAA of a series of partially reacted OMPs indicates that the TBT-substituted esters partially decompose during one year of storage at -78 °C, but mass sensitive SEC-ΔRI indicates that the polymer backbone remains intact. Comparison of SEC-GFAA and SEC-ΔRI suggests a convenient chromatographic method for determining reaction kinetics of both MMA and TBTM simultaneously.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Acetic acid; adsorption; differential refractive index; fractionation; graphite furnace atomic absorption; kinetics; methyl methacrylate; organometallic copolymer; SEC; stability; tributyltin acetate; tributyltin methacrylate.

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

30

15. Price

$7.50

USCOMM-DC 6043-P80