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CHARACTERIZATION OF ORGANOMETALLIC COPOLYMERS AND COPOLYMERIZATION BY SIZE-EXCLUSION CHROMATOGRAPHY COUPLED WITH TRACE METAL- AND MASS-SENSITIVE DETECTORS

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SUMMARY

An important class of controlled-release, biocidal triorganotin-containing copolymers (OMPs) is produced by the free radical initiated reaction of a triorganotin methacrylate (typically tributyltin methacrylate, TBTM) with methyl methacrylate. In earlier studies, we have demonstrated that size-exclusion chromatography (SEC) on μStyragel, coupled with an in-line graphite furnace atomic absorption detector (GFAA) quantifies at least two well-resolved tin-bearing molecular weight fractions observed in many different commercial OMP formulations: a polymer fraction, and, probably, unreacted TBTM. When tetrahydrofuran is used as the eluent, a third component, believed to be an ionic tin-containing compound, is adsorbed and slowly eluted. We now verify that a dilute solution of acetic acid in the tetrahydrofuran efficiently desorbs this species.

If a one percent solution of acetic acid in tetrahydrofuran is introduced into the mobile phase as a discrete, injected volume several minutes after the injection of the polymer formulation, there appears in the SEC–GFAA chromatogram: the polymer peak, the monomer peak, several minutes of tailing, and, finally a spike, with little additional tailing.

However, when a one percent solution of acetic acid in tetrahydrofuran is used as the eluent, the high polymer peak is substantially reduced in size owing to acid hydrolysis of polymeric esters to which the tributyltin is chemically bonded; the low-molecular-weight peak is substantially increased. Thus, delayed injection of acetic acid serves the purpose of avoiding acid hydrolysis of the polymer.

In the work described, only trace amounts of acetic acid (0.5 μl to 5.0 μl) were introduced by injection into the tetrahydrofuran mobile phase, whereas prolonged exposure to dilute solutions of acetic acid in tetrahydrofuran —*e.g.*, introduced by a gradient method— could be expected to shorten column life.

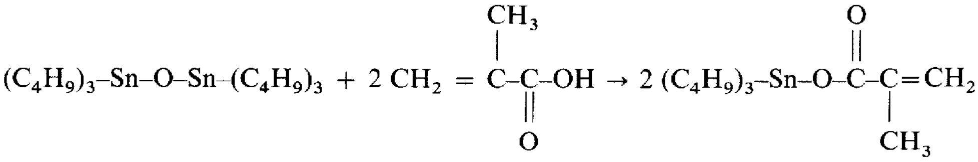
Partial decomposition of esters was found in partially reacted OMPs after one year of storage at −78°C.

INTRODUCTION

The free-radical initiated addition of triorganotin methacrylate with methyl methacrylate (MMA) results in a copolymer in which toxic tin-bearing moieties are chemically bonded to carbonyl groups pendant from the polymer backbone[1]. Organometallic polymers (OMPs) of tributyltin methacrylate (TBTM) and MMA, when incorporated into paints on the hulls of ships retard fouling in marine environments for long periods of time[2]. The degradation of the polymer in the service environment and its protective mechanisms are complex, as the macromolecular materials break down slowly, with diffusion of low-molecular-weight (low-MW) species and slow release of the toxic tin-containing moieties[1–3].

In previous studies[4–7] we have demonstrated by means of size-exclusion chromatography (SEC) coupled with graphite furnace atomic absorption spectroscopy (GFAA) that numerous experimental and commercial OMP formulations in dilute solutions of tetrahydrofuran (THF) were always separated into two well-resolved major tin-bearing fractions of widely different molecular weight. Elution of these two fractions is followed by the elution of a tailing species containing tin. This tailing was not quantified but was attributed to a cationic tin-bearing species (possibly tributylin cation, TBT^+) adsorbed on the SEC packing (μStyragel)[6,9].

The presence of TBT^+ in the chromatograms of OMP formulations is uncertain, but might result from dissociation of: (1) the TBTM ester during or following synthesis from TBT oxide and methacrylic acid, which generates water (eqn. 1);



$$(C_4H_9)_3\text{–Sn–O–Sn–}(C_4H_9)_3 + 2\,CH_2 = \overset{\overset{CH_3}{|}}{C}\text{–}\underset{\underset{O}{\|}}{C}\text{–OH} \rightarrow 2\,(C_4H_9)_3\text{–Sn–O–}\overset{\overset{O}{\|}}{C}\text{–}\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \quad (1)$$

(2) the polymeric tributyltin ester during synthesis of the copolymer from TBTM and MMA; (3) the copolymer during chromatography by an unknown mechanism; or all of these mechanisms. It has been determined[3] that an OMP terpolymer similarly prepared from tripropyltin-, tributyltin-, and methyl methacrylates when leached out into water yields both of the triorganotin cations, though probably at different rates. After an early period of rapid release, leaching follows a zero order rate law[3]. In order to understand the leaching mechanism and specify controls over the governing molecular properties, it is necessary to quantify the high- and low-MW species (*e.g.*, polymer, TBTM, and the adsorbed species) and differentiate between them. The present research shows that dilute solutions of acetic acid effect desorption of a tin-containing species from μStyragel, probably with *in situ* derivatization, ion-pairing, or neutralization.

INSTRUMENTAL METHODS*

The high-performance liquid chromatography–ultraviolet (UV)/refractive index (RI) detector–GFAA system[10] is outlined schematically in Fig. 1. A high-

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* 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.

pressure pump (Altex Model 110A, Berkeley, CA, U.S.A.) equipped with a single piston was used to deliver solvent at a controlled flow-rate (0.5 ml min^{-1} or 1.0 ml min^{-1} in the present work) under isocratic conditions. Solutions of organometallic compounds, or compounds of standard MW, were injected (50 μl or 500 μl) into the SEC system by means of an on-line high pressure syringe loading sample injection valve (Altex Model 70-10). An in-line precolumn filter, pore size 2 μm (No. 84560; Waters Assoc., Milford, MA, U.S.A.) protected columns employed for SEC. The columns contained a porous, highly divinylbenzene cross-linked polystyrene (μStyragel, Waters Assoc.) having a particle size of 10 μm, nominal pore size 10^3 Å. Either a single column or three columns in series were employed. The column dimensions were 300 × 7.8 mm O.D. Columns were connected by 100 × 1.5 mm O.D. × 0.2 mm I.D. stainless-steel tubing, and to a fixed-wavelength (254 nm) UV/ΔRI dual detector (Knauer, Utopia Instruments, Joliet, IL, U.S.A.). For experiments in which the ΔRI detector was employed, the temperature was maintained at 22 ± 0.1°C by means of a thermostatted water bath (Lauda K4R circulating constant temperature bath, Brinkman, Westbury, NY, U.S.A.). Columns were maintained at room temperature (22°C). Medium-walled PTFE tubing (1.6 mm O.D., 0.7 mm I.D.) transported effluent from the UV/ΔRI detector cell outlet to a specially constructed PTFE "well sampler" described previously[10]. Aliquots of 20 μl were automatically withdrawn at 49.2-sec intervals (Δt), in those experiments involving SEC automatically coupled to GFAA.

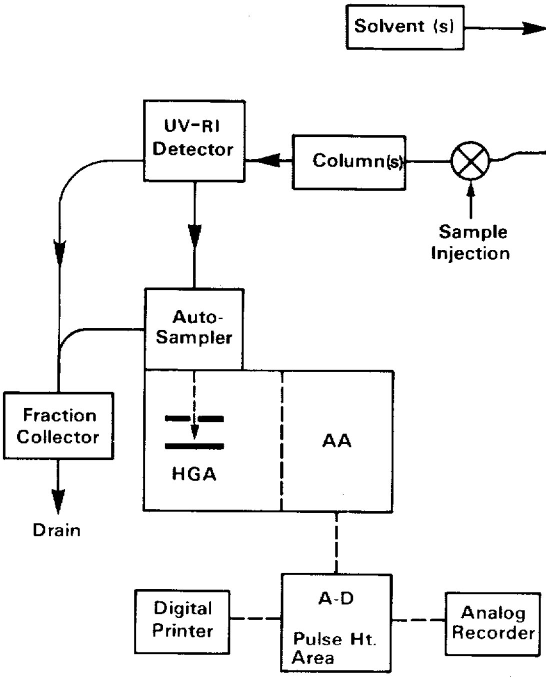


Fig. 1. Block diagram summarizing the SEC–UV/ΔRI—GFAA system, including accessory devices. In the present work, either the auto-sampler continuously transferred 20-μl specimens into the graphite furnace at 49.2-sec intervals, or fractions were collected after elution for subsequent quantitation of tin. AA = Atomic absorption; A-D = analog-to-digital converter; HGA = heated graphite atomizer.

Since the GFAA detector is about two orders of magnitude more sensitive to organotin polymers in THF than the ΔRI detector[4], correspondingly greater quantities of polymer are required to obtain ΔRI chromatograms than GFAA chromatograms. Fractions of the eluent emerging from the UV/ΔRI detection cell were collected in glass vials in small volumes (0.5 ml), transferred individually to polystyrene cups (Perkin-Elmer, Norwalk, CT, U.S.A.), diluted with THF to the extent necessary to keep the atomic absorption readings in the linear absorbance range, and sampled two or more times by transferring 20 μl aliquots to the GFAA furnace. In this way, an average of two or more readings were observed on each collected fraction. Following these SEC–ΔRI–GFAA experiments, the SEC–ΔRI chromatography was repeated at a higher sample concentration (2.0 %, w/v) to obtain better than threshold definition of discrete fractionated species found in relatively low concentration. The more time-consuming sample collection and analysis by GFAA was not repeated.

A Perkin-Elmer model 360 dual beam atomic absorption spectrometer with deuterium lamp background correction and a Model 2100 graphite furnace atomizer were used for specific element detection. GFAA conditions: wavelength 224.6 nm; drying time, 10 sec, 100°C; charring time 10 sec, 200°C; atomization time 10 sec, 2700°C; atomization interval 49.2 sec. In GFAA chromatograms, the observed peak heights represent measured absorbances due to the concentrations of tin contained in a 20-μl aliquot. At a flow-rate of 1.0 ml min^{-1}, 2.43 % of the total effluent is sampled; at 0.5 ml min^{-1}, 4.86 %.

An automatic digital integrator was used to obtain a direct record of atomic absorption intensities (either an Infotronics Model CHS-204, Infotronics, Austin, TX, U.S.A. or a Shimadzu Model C-RIA integrator printer, Columbia, MD, U.S.A.). Peak areas in SEC–GFAA chromatograms were calculated by summing up the recorded intensities of individual tin-specific GFAA peaks[10,11]. Peak areas in one series of ΔRI chromatograms were measured by digital planimetry, using a Hewlett-Packard (Palo Alto, CA, U.S.A.) Model 9810A planimeter, fitted with a Model 9864A digitizer.

Samples and reagents

Samples of a copolymer of TBTM and MMA (OMP-2) were provided as a 50 % solution in benzene by the David Taylor Naval Ship Research and Development Center, Annapolis, MD, U.S.A. This copolymer is prepared by the reaction of TBTM and MMA in 1:1 molar proportions by refluxing in reagent-grade benzene (polymer to solvent ratio 1:2, w/v), as described by Dyckman and Montemarano[12]. The suggested copolymer formula is depicted in Fig. 2. The TBTM was prepared from highly purified TBT oxide and methacrylic acid[8]. MMA, commercially prepared and inhibited with 25 ppm hydroquinone, was used as received. The preparation of partially reacted samples is described in detail in our earlier paper[6]. These samples were maintained for one year at -78°C in THF (10 % solutions) before running the SEC–GFAA and SEC–ΔRI chromatograms discussed in the present research, and quantifying tin in collected fractions.

In several experiments, the injected volume and/or the chromatographic eluent consisted of THF containing reagent-grade acetic acid. The amounts and concentrations of injected solutions and the methods of introducing acetic acid into the flowing stream of THF are indicated in legends to the appropriate figures.

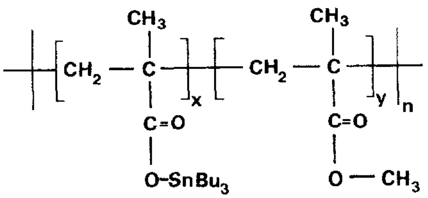


Fig. 2. The suggested formula of a copolymer prepared by the free-radical addition of TBTM to MMA. The subscripts x, y and n represent numbers of monomers. Neither the numbers x, y, or n, nor the tacticity of the copolymer is assumed to be constant.

All solvents were purified before use by filtration (0.5-μm solvent clarification kit; Millipore, Bedford, MA, U.S.A.) and degassed by magnetic stirring at ambient temperature under a vacuum. Insoluble materials were removed from sample solutions in THF by filtration (0.45-μm organic sample clarification kit, Millipore).

Samples of polystyrene serving as MW standards were obtained from Arro Labs., Joliet, IL, U.S.A., dissolved in THF (50 μg/50 μl) and eluted with the same solvent.

Analysis of data

In order to determine the conversion of monomer to polymer in the partially reacted samples, high- and low-MW peaks were quantitated either by (a) summing observed tin-specific GFAA signals[10,11] or (b) determining peak areas in ΔRI chromatograms by digital planimetry. The SEC columns were calibrated with polystyrene standards, detected by UV absorption at 254 nm. Calibration curves prepared for systems of either one or three columns exhibited a linear coefficient of correlation greater than 0.99 between log MW of the polystyrene samples and the elution volume. A typical calibration curve may be seen in an earlier study[5].

The ΔRI chromatogram of the partially reacted copolymers typically exhibited a differential peak of high MW (a "positive" peak) followed by a second peak having the same sign, attributed to low-MW species, and a third peak of opposite sign. In calculating the ratio of high- and low-MW species, we considered only the areas of the first two peaks. The third peak presumably is due to additives to TBTM and MMA; differences in the area of this peak from sample to sample are not related to the extent of reaction.

Sample recoveries were calculated for SEC–GFAA chromatograms by summing all of the tin signal observed and comparing the sum with that expected for a given injection. The fraction of eluent actually sampled depends on the flow-rate and the frequency of sampling (indicated automatically by the digital integrator).

For experiments involving total collection of eluent, the collected fractions, tested individually by GFAA with appropriate dilution (THF) were summed over the entire chromatogram and compared with the original sample following necessary dilution. In this case, recoveries of approximately 100 ± 10% were obtained.

RESULTS AND DISCUSSION

Fig. 3 depicts the SEC–GFAA chromatogram of a sample of OMP-2 dissolved in THF (1.0%, w/v) and eluted with THF through a single 10^3 Å μStyragel column.

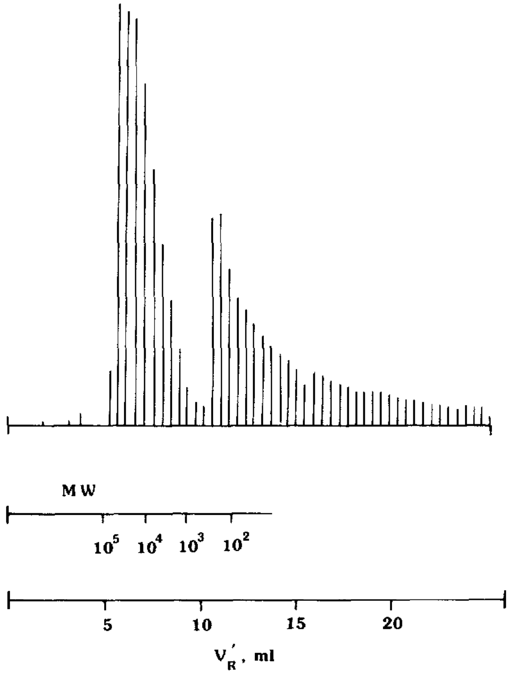


Fig. 3. SEC–GFAA chromatogram of OMP-2. Solvent, THF. Column, μStyragel (one), average pore size 10^3 Å. Mobile phase, THF. Flow-rate 0.5 ml min^{-1}. Detector, Perkin-Elmer 360, equipped with an Sn-specific EDL lamp operating at 224.6 nm. Injected volume 50 μl. Injected concentration: 50 μg/50 μl.

TABLE I

EFFECTS OF ACETIC ACID, INTRODUCED BY SEVERAL METHODS, ON ADSORBED TIN-BEARING SPECIES DURING SEC–GFAA OF OMP-2

Fractions: A: MW = 100,000–1000 daltons, according to calibration; B: MW = 500–100 daltons; C: Adsorbed species, tailing.

Solvent	*Mobile phase*	*Percent of injected tin recovery*			*Apparent total recovery (%)**
		Fraction			
		A	*B*	*C*	
THF	THF	27.7	8.6	12.9	48.5
THF, 0.1% acetic acid	THF	44.3	12.6	15.6	72.5
THF, 1% acetic acid	THF	24.8	14.5	0.8	40.2
THF	THF, 1.0% acetic acid	15.1	60.0	2.8	78.0
THF	THF**				
	(a)	46.6	31.2	1.0	78.9
	(b)	45.3	12.0	27.5	84.9
	(c)	43.6	10.6	40.7	95.0

* Eluted Sn as a percentage of injected Sn.

** 50 μl of 1.0% acetic acid in THF injected after a delay of (a) 0.5 ml after sample injection, (b) 2.0 ml after sample injection, (c) 4.0 ml after sample injection.

At the flow-rate of 0.5 ml min^{-1}, the mixture is separated into the expected[4-6] high- and low-MW fractions. Prolonged tailing of adsorbed tin-bearing species accounts for at least 26.7% of the observed tin (Table I). Their elution is not complete but would have required hours at the same flow-rate. At this concentration, the 50 μl injection included about $1.3 \cdot 10^{-7}$ mole of the tailing species if the latter is assumed to be TBT$^+$.

Fig. 4A represents the SEC–GFAA chromatogram of a specimen of the same sample, dissolved in THF and injected (50 μl) 1.0 h after adding 1.0% (v/v) of glacial acetic acid ($10.4 \cdot 10^{-7}$ mole per 50 μl of injected solution). Fig. 4B represents the SEC–GFAA chromatogram of a similar specimen to which was added 0.1% (v/v) of acetic acid ($1.0 \cdot 10^{-7}$ mole per injection). The net results show a higher quantity of

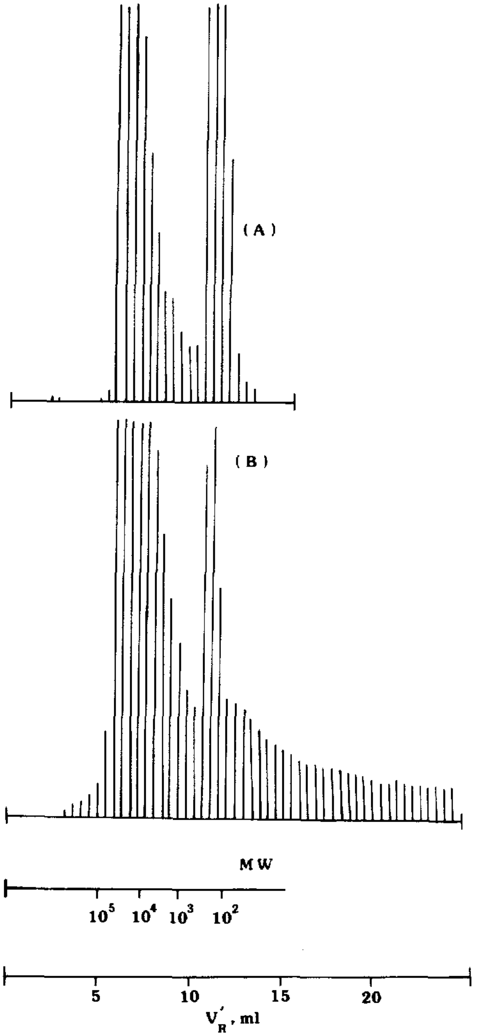


Fig. 4. SEC–GFAA chromatograms of OMP-2. (A) Solvent, THF containing 1.0% (v/v) acetic acid; acid added 1.0 h prior to injection. All other conditions as for Fig. 3. (B) Solvent, THF containing 0.1% (v/v) acetic acid; acid added 1.5 h prior to injection. All other conditions as for Fig. 3.

tin-bearing species eluted in the presence of 0.1 % acetic acid than that eluted by THF alone, and a somewhat higher relative quantity in the low-MW peak; tailing is not terminated but continues for a long period of time. With 1.0 % acetic acid, there results an abrupt termination of tailing, with pronounced enhancement of the low-MW peak (Fig. 4A).

When the eluent is changed, from THF to THF containing 1.0 % acetic acid, the SEC–GFAA peak due to the high-MW tin-bearing species is markedly diminished in size, with a corresponding increase in the low-MW peak (Fig. 5 and Table I).

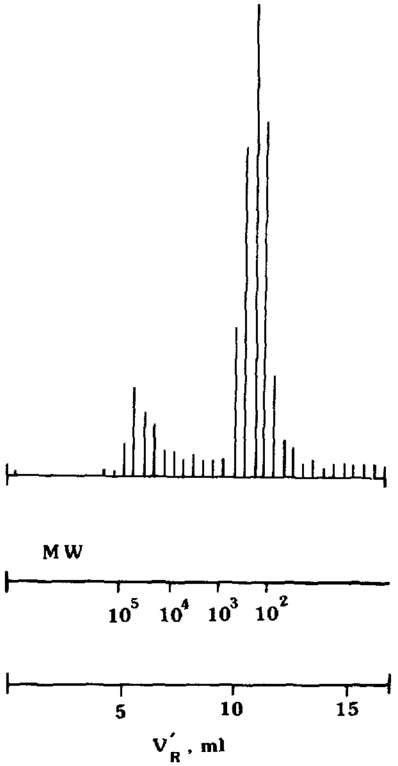


Fig. 5. SEC–GFAA chromatogram of OMP-2. Solvent THF. Mobile phase THF containing 1.0 % (v/v) acetic acid. All other conditions as for Fig. 3.

We interpret these data to indicate the formation of a neutral tin-containing species, which coelutes with neutral TBTM. In the case of the mixture of 1.0 % polymer and 1.0 % acetic acid in THF, the cationic tin-containing compound may be either neutralized by acetate anions or displaced by protons. In the case of elution with THF containing 1.0 % acetic acid, TBT esters of the carboxyl groups pendant from the polymer backbone also are hydrolyzed by the acid, releasing a large portion of the polymeric TBT in the form of TBT^+ via an exchange reaction. Tailing in the latter chromatogram is due to continued hydrolysis of the polymer as it traverses the length of the column.

Desorption involves acid–base equilibria rather than stoichiometric reactions. For example, 50 μl of 0.1 % acetic acid coinjected with the solution of OMP-2 includes sufficient acetate anions, dissociated or associated with protons, to react with almost all of the adsorbed TBT^+ observed in Fig. 3. The fact that the excess acetate anions available in the 1.0% solution was required to terminate tailing indicates a complex equilibrium involving TBT^+, H^+, acetic acid, TBT acetate, acetate anion, with probable association of an electron-deficient cation with the electron rich aromatic rings of the packing material.

In order to characterize organometallic polymer formulations by SEC-GFAA, hydrolysis of the polymer fraction must be avoided. Again, it is essential not to overestimate the peak attributed to unreacted TBTM. TBTM (MW 375) is not distinguishable from TBT acetate (MW 337) in Figs. 4 and 5, where polymer, TBTM,

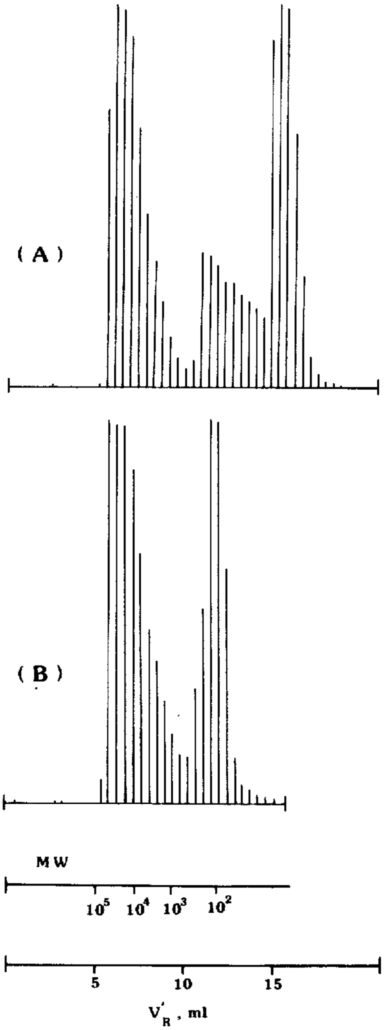
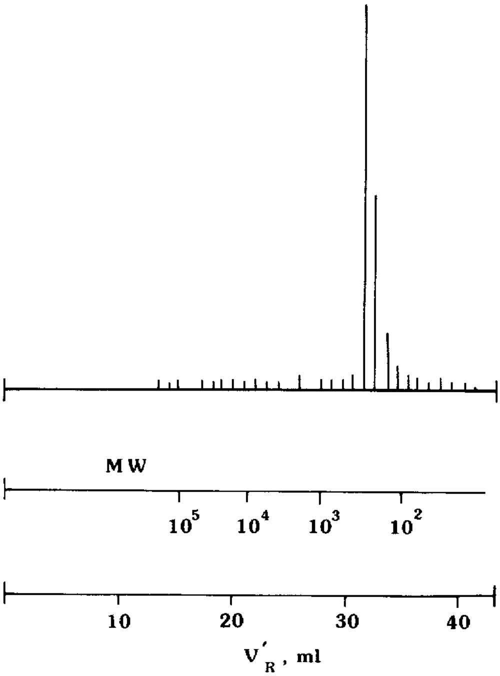


Fig. 6. SEC–GFAA chromatograms of OMP-2. (A) Solvent THF. Mobile phase THF. 50 μl of THF containing 1.0% acetic acid introduced into the mobile phase 8.0 min (4.0 ml) after injection of the OMP solution. All other conditions as for Fig. 3. (B) As (A), except that 50 μl of 1.0% acetic acid in THF was introduced 1 min (0.5 ml) after the solution of OMP-2.

TBT$^+$, and acetic acid were injected at the same time. Therefore, we injected initially a 50-μl solution of the polymer mixture in THF, followed after a measured delay by a 50-μl injection of the dilute acid. The results (Fig. 6 and Table I) show that sufficient acetic acid, injected at any time after the polymer formulation, causes termination of tailing with an intense tin peak corresponding to the expected time of elution of totally permeating acetic acid.

Even with delayed injection, however, there remains the problem of distinguishing between neutral tin-bearing species and tin-bearing cations, a particularly important distinction in the kinetic analysis of the copolymerization reactions[6].

In a previous report, however[7] we demonstrated that purified TBTM in THF solution is eluted from three μStyragel columns in series within the narrow elution volume corresponding to the MW range of about 500 to 100 daltons without significant tailing (Fig. 7). Fig. 7 provides strong though somewhat empirical evidence that neutral esters which participate in the copolymerization reaction are characteristically included in this particular MW range. Further support is evident in the excellent fit to kinetic rate laws of points based on the conversion of TBTM so determined (Fig. 8). Some of the raw data are presented in Fig. 9 and the reduced data are summarized in Table II.



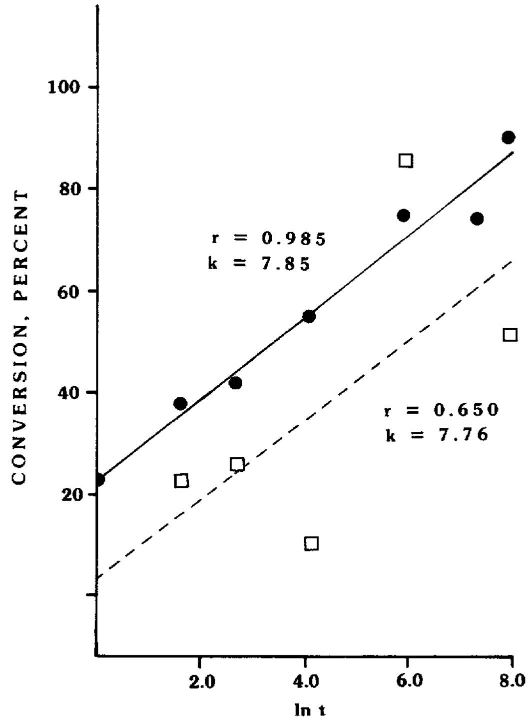


Fig. 7. SEC–GFAA chromatogram of TBTM purified by recrystallization from light petroleum (b.p. 35–60°C). Solvent, THF. Mobile phase, THF. Columns, μStyragel (three) in series; average pore size 10^3 Å. Flow-rate 1.0 ml min^{-1}. Injected volume, 50 μl. Injected concentration of TBTM, 50 μg/50 μl. GFAA detector, Perkin-Elmer 360.

Fig. 8. ●, 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 Fig. 9. □, Conversion of TBTM, as calculated from data obtained after one year of storage at −78°C, including the chromatograms depicted in Fig. 10.

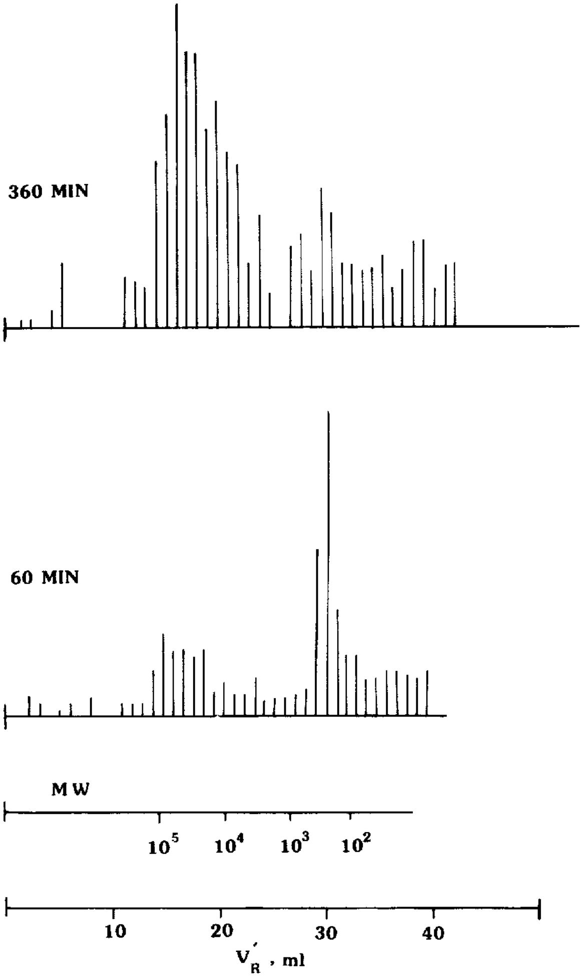


Fig. 9. SEC–GFAA chromatograms of partially reacted specimens aliquotted during the copolymerization of TBTM and MMA. Solvent, THF. Mobile phase, THF. Flow-rate, 1.0 ml min^{-1}. Columns, μStyragel (three), average pore size 10^3 Å. All other conditions as for Fig. 3.

Because data collection on the samples used to obtain Fig. 8 was not continued to the complete extinction of tailing, we decided to reexamine several of the partially reacted samples, now after one year of storage at −78°C. Chromatography performed on one column rather than three, with collection of fractions and delayed injection of acetic acid, gave the histograms plotted in Fig. 10. The conversion and recovery data are summarized in Table III. While the calculated tin recovery is usually 100 ± 10%, the extent of apparent conversion is quite different from that obtained originally (compare Fig. 8, broken line, with original data, solid line). The very irregular changes in the distribution of tin and the very large quantities of TBT acetate indicate that decomposition of esters was extensive, even at the temperature of dry ice.

On the same column we injected increased sample concentrations (1 mg in 500

TABLE II

CONVERSION OF TBTM TO COPOLYMER AS INDICATED BY SEC–GFAA

Fractions: A: MW = 100,000–1000 daltons, according to calibration; B: MW = 500–100 daltons; C: adsorbed species.

Reaction time (min)	*Percent of injected tin recovered*			*Calculated conversion (%)**	*Apparent recovery (%)***
	Fraction				
	A	*B*	*C*		
0	6.9	23.1	21.1	22.9	51.2
5	9.8	16.1	8.7	38.0	34.7
15	25.9	36.4	12.8	41.6	75.0
60	10.0	8.1	5.6	55.3	23.7
360	22.8	6.9	14.2	76.7	44.0
1440	(70.8)	(25.0)	(4.1)	(73.9)	–***
2880	26.0	3.1	0.40	89.5	29.5

* Conversion (%) = $\frac{\text{A}}{\text{A + B}} \times 100$.

** Eluted Sn as a proportion of injected Sn.

*** Amount of tin injected not determined.

μl instead of 50 μg) in order to follow changes in mass distribution as a function of time by means of SEC–ΔRI chromatograms. Typical chromatograms are presented in Fig. 11. The results, summarized in Table IV and plotted in Fig. 12, exhibit a very high linear correlation between the log of reaction time and the extent of mass conversion, especially during the first 360 min of reaction. These data indicate that the polymer backbone itself probably is not decomposed on storage. It is also apparent that the high- and low-MW fractions are retained and eluted primarily by the SEC mechanism, whereas tailing, in SEC–GFAA chromatograms, is due to adsorptive retention. These differences in mode of retention point to species of different polarity, again supporting the attribution of tailing to TBT^+ cations.

Sample recovery

The data in Table III show that tin recovery is essentially complete in the case of injection where tailing is terminated with acetic acid, and the eluent is totally collected. Deviations from 100% result from such experimental variables as deterioration of furnace tubes and contact rings, and possibly deviation from linearity over the total range of Sn concentrations examined.

Errors in the SEC–GFAA chromatograms of OMP-2, obtained with automatic sampling of eluent (Table I) result from several factors. Some of the GFAA peaks were out of the range of linear absorbance response, so that the apparent recovery is low. Elution of the derivative occurs with a very narrow retention volume, so that a portion of this peak having much higher than average intensity may be eluted between sampling intervals; and finally some of the chromatograms are not continued to the termination of tailing.

The fact that hours of elution would be required to desorb all of the tin-

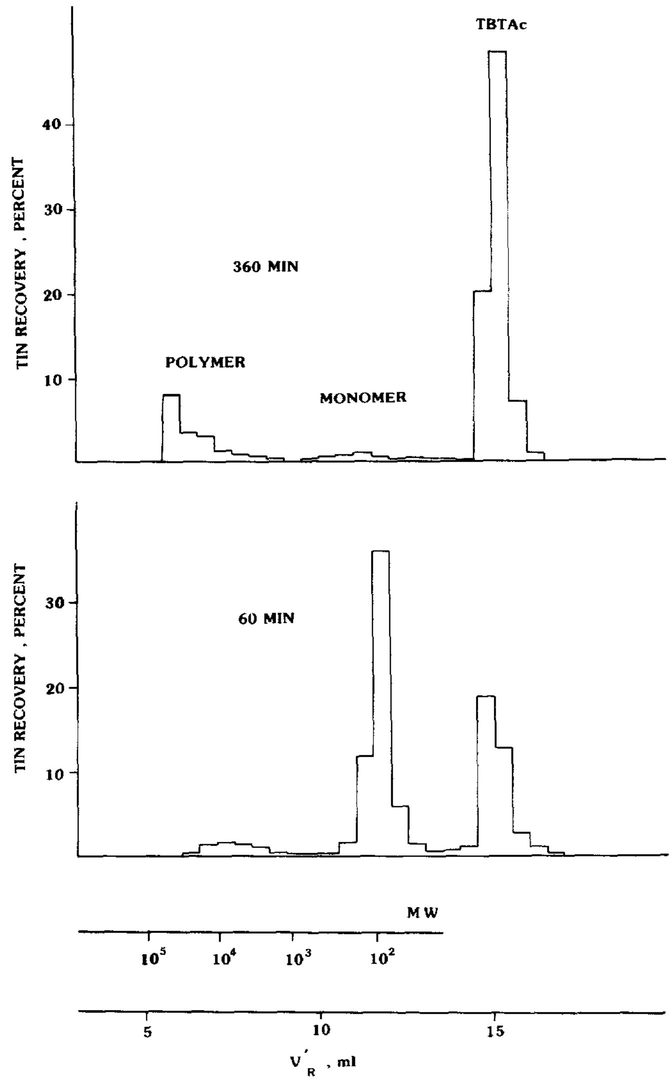


Fig. 10. Partially reacted specimens retested after one year of storage at −78°C. Histogrammic peak height indicates tin content of fractions. Solvent, THF; mobile phase, THF. Flow-rate 0.5 ml min^{-1}. Column, μStyragel (one), pore size 10^3 Å. Injected volume, 500 μl. Injected concentration 100 μg/500 μl. 500 μl of 1.0% acetic acid in THF introduced by injection 8 min (4.0 ml) after the injection of polymer.

containing species in the absence of acetic acid emphasizes the importance of such an elution aid in the chromatography of polar organometallic or ionic macromolecules by the size exclusion mode.

Related SEC–GFAA

The only directly comparable research described in the literature, to our knowledge, is that of Weiss *et al.*[12], in the SEC–GFAA of shale oil containing arsenic. They found, after the delayed injection of a trace of methanol into the THF mobile phase,

TABLE III

DISTRIBUTION OF TIN IN COPOLYMER SOLUTION DETERMINED BY SEC–GFAA AFTER ONE YEAR OF STORAGE AT −78°C

Fractions as in Table II.

Reaction time (min)	*Percent of injected tin recovered*			*Calculated conversion (%)**	*Apparent recovery (%)***
	Fraction				
	A	*B*	*C*		
5	15.0	47.9	41.1	23.9	104.0
15	8.1	24.1	58.6	25.1	91.1
60	9.5	86.3	59.4	9.8	155.0
360	18.8	3.3	87.8	85.0	110.0
2880	12.1	11.0	61.4	52.5	84.6

* Conversion (%) $= \frac{A}{A + B} \times 100.$

** Eluted Sn as a proportion of injected Sn.

that the observed arsenic peak was split into two parts, the second peak corresponding in elution time to the measured delay. Whether this desorption resulted from physical interaction or derivatization of adsorbed species was not determined. In principle the technique of delayed injection of a trace amount of a derivatizing or desorbing agent will be advantageous whenever the system cannot tolerate co-injection and/or greater than trace quantities of the injected species, *e.g.*, when the additive might react with coinjected materials or may be incompatible with packing materials with the attendant risk of shortened column life.

The comparison of kinetic results based on SEC–GFAA and SEC–ΔRI chromatography in tandem is the subject of continuing study.

CONCLUSIONS

Element-specific SEC–GFAA is an analytical technique of demonstrated value for characterizing copolymers having triorganotin moieties chemically bonded to carboxyl groups pendant from the polymer backbone. SEC–GFAA associates tin content with two well-resolved fractions of high and low MW. The present results verify that a third component in substantial amounts is present in a typical organotin polymer formulation. It is adsorbed on μStyragel when THF is the chromatographic eluent and quantitatively desorbed when acetic acid is introduced into the mobile phase. The adsorbed species is ascribed to TBT^+ and the on-column derivative to TBT acetate.

Although the triorganotin esters are subject to acid hydrolysis by acetic acid, this hydrolysis is avoided by adding the acetic acid to the mobile phase at a measured time after introduction of the polymer formulation. Thus acid does not come into contact with species eluted prior to totally permeating species.

Reexamination of partially reacted polymer formulations after storage at −78°C showed surprisingly extensive degradation of the polymer esters, but not polymer chains.

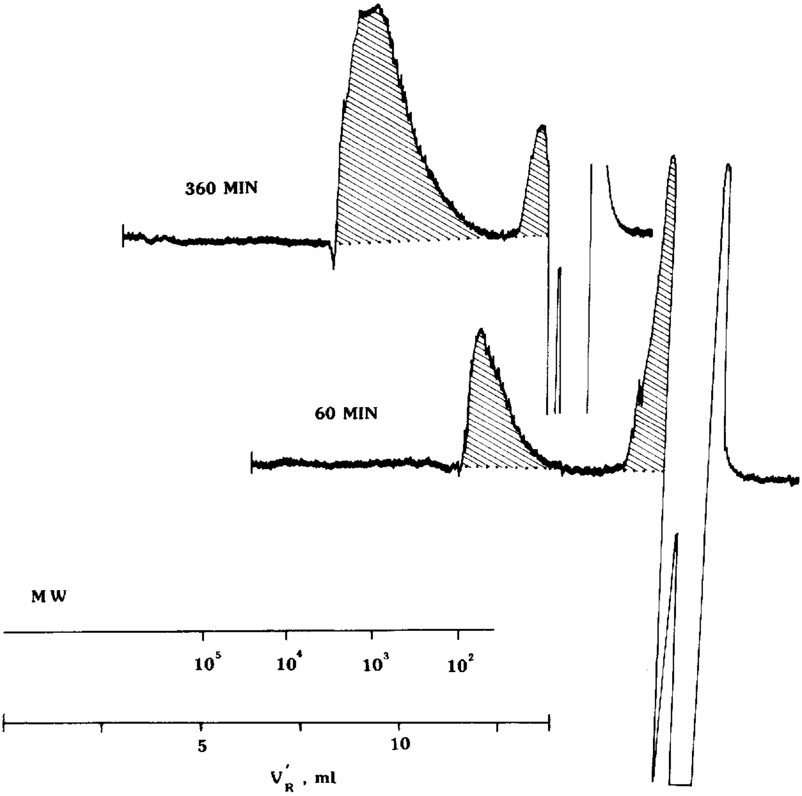


Fig. 11. SEC–ΔRI chromatograms of samples taken during the copolymerization of TBTM and MMA and stored one year at −78°C. Solvent, flow-rate, mobile phase and column as for Fig. 10. Detector, Knauer dual detector; ΔRI sensitivity, $0.5 \cdot 10^{-6}$ ΔRI units = full scale deflection. Injected volume 500 μl. Injected concentration 1000 μg/500 μl.

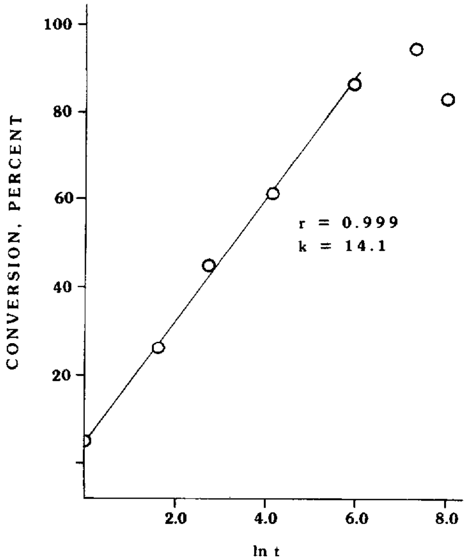


Fig. 12. Conversion of low-MW to high-MW material mass during the copolymerization of TBTM and MMA, plotted as a function of the time of reaction. Conversion data calculated from chromatograms including those in Fig. 11.

TABLE IV

CONVERSION OF MONOMER TO POLYMER AS DETERMINED BY SEC–ΔRI

Fractions: A: MW = 100,000–1000 daltons, according to calibration; B: MW = 500–100 daltons; C: "Negative" peak.

Reaction time (min)	*Fraction**			*Calculation conversion (%)***
	A	*B*	*C*	
0	0.58	11.81	10.77	4.7
5	6.77	19.03	0.39	26.2
15	14.77	17.74	6.26	45.4
60	26.84	16.90	5.55	61.4
360	44.71	6.19	7.23	87.8
1440	33.36	2.84	6.38	92.1
2880	13.29	2.84	11.80	82.4

* Areas in cm^2 as determined by planimetry.

** Conversion (%) $= \frac{A}{A + B} \times 100.$

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