NBSIR 81-2424

Characterization of Organometallic Polymers by Chromatographic Methods and Nuclear Magnetic Resonance

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

December 1981

Prepared for

Naval Ship R & D Center
Annapolis Laboratory
Annapolis, MD 21402

NBSIR 81-2424
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CHARACTERIZATION OF ORGANOMETALLIC POLYMERS BY CHROMATOGRAPHIC
METHODS AND NUCLEAR MAGNETIC RESONANCE

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Abstract

Organometallic polymers (OMP) are an increasingly important class of
marine surface antifouling agents undergoing intensive development by the U.S.
Navy. Commercial procurement of such polymers, expected in the near future,
will require Mil Specs designed to assure reproducibility between batches in
order to achieve satisfactory reliability in service. New analytical methods
are needed in writing such Mil Specs. Candidate OMP's have been characterized
at NBS by size exclusion chromatography (SEC) coupled with tin-specific graphite
furnace atomic absorption spectroscopy (GFAA) as well as by Fourier transform
nuclear magnetic resonance (FT-NMR). The key molecular parameters of many
OMP's, the kinetics of formation of a typical copolymer, and the effects of
different concentrations of free radical initiators on the formation of a
copolymer in a well-stirred reaction system have all been characterized by
means of SEC-GFAA chromatograms. FT-NMR spectra of ^{119}Sn have given kinetic
information in good agreement with that obtained by SEC-GFAA. Both chemical
shift and linewidth of the tin NMR signal have been shown to have an unusually
large solvent and temperature dependence. Directions for future research on
OMP's are discussed.

Key words: Atomic absorption spectroscopy; biocide; chromatography; copolymers; kinetics; NMR; organometallic polymers; polymers; size exclusion chromatography; slow-release antifoulant; tin.

1.   Background

Organometallic polymers (OMP's) prepared from esters of methacrylic acid and triorganotin methacrylate provide a linear chain molecule incorporating pendant biocidal organotin moieties [1]. Coated on ship hulls, polymers prepared from methylmethacrylate (MMA) and tributyltinmethacrylate (TBTM) provide years of antifouling protection in the marine service environment [2]. The long-term reliability of organotin-containing coatings in service can only be assured if there is adequate reproducibility of the coating materials from lot to lot. "Reproducibility" in this context means much more than the usual analytical measurements such as viscosity, percent tin, etc. The assurance of adequate quality control may demand, in the final Mil Spec, requirements for average molecular weight (M_w or M_n); molecular weight distribution, MWD; maximum allowable concentration of low MW tin-containing polymer and/or monomer; and possibly other less conventional measures of polymer properties as well. The copolymer composition equation [3] (Eq. 1), is a logical starting point. According to this equation, the initial concentration of two reacting monomers, A and B, and their relative reactivity ratios, r_1 and r_2, determine the ratio of components in the copolymer, given ideal behavior:

$$\frac{dA}{dB} = \frac{[A]}{[B]} \frac{r_1[A]/[B] + 1}{[A]/[B] + r_2} \tag{1}$$

Ghanem et al. [4] determined, from empirical Fineman-Ross slopes [5] based on the composition of copolymers prepared with TBTM and MMA in different ratios, that the reactivity of TBTM compared to MMA is 0.79 to 1.00 and that the reaction did exhibit almost ideal behavior. Their copolymers were prepared in sealed tubes at 60.1 °C with azobisisobutyronitrile (ABIN) (0.2 percent by weight) as initiator.

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The synthesis of organometallic polymers is usually performed under very different conditions in organic solvents [1,6], with stirring. Assuming that Ghanem's reactivity ratios remain constant under dissimilar reaction conditions, ideally one could simply continue the polymerization of preselected concentrations of the monomers until all monomeric material became fully incorporated into a polymer possessing the desired ratio of TBTM and MMA. For optimal performance, the polymer would exhibit a narrow molecular weight dispersion (MWD) and a molecular weight (MW) probably in the range of 100,000 daltons [6], with little or no remaining TBTM or MMA and without substantial homopolymerization of either species.

Apart from the difficulties imposed by different reaction conditions, several side reactions probably complicate the applicability of Eq. (1) to real systems. Homopolymerization of TBTM, evident in chromatographic data earlier reported by us [7] and/or homopolymerization of MMA would alter the ratio of the end groups that are susceptible to free radical activation and addition, altering [A] and [B] in the composition Eq. (1), and hence the composition of the resultant copolymer. This would, at worst, result in significant bimodal polymerization. Reaction of TBTM or MMA may be complicated by side reactions depleting one or the other monomer, e.g., hydrolytic fragmentation of TBTM or oxidation of MMA. Reaction of PMMA or of MMA with oxygen results in low MW peroxides, formaldehdye, and methyl pyruvate [8]. To our knowledge, no data currently indicate that TBTM or the copolymer is similarly oxidized. Inhibitors are available to retard oxidation of the copolymer.

It is not asserted here that all of these complications actually occur during the formulation of an organometallic copolymer, but rather that a practical method or methods for characterizing the copolymer and/or the copolymerization process is a prerequisite for understanding and controlling the rates of addition of different monomers comprising the copolymer.

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Jewett et al., for example [9], determined that tributyltin cations leach into water from organotin polymer paints. Initial rapid leaching is followed by the slower zero order mechanism observed by others [1]. The chemical and physical processes of coating decomposition have not been conclusively demonstrated. Possibly the slow release mechanism is a result of continuing hydrolytic scission of polymeric ester groups with migration of the freed tributyltin moieties to the polymer surface, but the initial rapid losses suggest a different process. Alternately or concurrently, the polymer coating may be slowly decomposed in service, constantly generating fresh surface by a self-polishing mechanism [10]. Reliability in long-term service probably requires a uniform mechanism of decomposition along linear polymer chains of a homogeneous polymer formulation. However, tin-specific chromatographic analysis of many OMP formulations invariably revealed low molecular weight, tin-bearing species [11]. This is undesirable from the viewpoint of controlling the release rate of toxic moieties. Long chain polymers are less mobile and less soluble than materials of the same composition but of low molecular weight. Thus, in addition to plasticizing effects, the more facile migration of low molecular weight species, e.g., TBTM monomers, introduces the risk of complicating mechanisms of release compared to a homogeneous formulation consisting only of long chain polymers.

For all of these reasons, a valid prediction of the performance of an OMP and its consequent environmental impact requires, at least, that knowledge of the manner in which it is formed must be obtained by methods permitting detailed molecular characterization. This detailed molecular characterization is essential to ensure reproducibility of the polymer between batches and its consequent reliability in use. The present report describes NBS research on the molecular characterization of current candidate OMP's and their polymerization process by chromatographic methods and nuclear magnetic resonance.

2. Experimental*

In two sets of experiments reported below, the conditions of sample preparation are varied: (1) a kinetic run, in which a mixture of TBTM and MMA, undergoing polymerization for a total period of 24 h, was sampled at predetermined intervals to provide partially reacted samples without interrupting the reaction process; and (2) a series of experiments in which copolymerization conditions were varied with respect to the concentration and the type of initiator added prior to copolymerization.

2.1 Chemicals

THF (Eastman-Kodak, Rochester, New York) was used throughout the chromatographic experiments as both solvent and eluent. The THF was purified by filtration before use (0.5 μm pore size filter) and degassed daily by magnetic stirring under a vacuum at ambient temperature. Reagent grade benzene was used as the copolymerization medium. Initiators (benzoyl peroxide and azobisisobutyronitrile) were of the highest available commercial grade.

Standard samples of polystyrene and a sample of poly(methylmethacrylate) are listed with their sources in table 1.

Deuterochloroform of stated isotopic purity 99.8 percent was obtained from Stohler Isotope Chemicals (Waltham, Massachusetts). Perdeuterobenzene of stated isotope purity 99.5 percent was obtained from Wilmad Glass Company (Buena, New Jersey). Tetramethyltin of stated purity 99.5 percent was obtained from Alfa Division, Ventron Corp., (Danvers, Massachusetts). All were used without further purification.

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*Certain suppliers of chemicals and equipment are identified by name in order to specify the experimental conditions adequately. This does not imply endorsement or recommendation by the National Bureau of Standards nor does it imply that the particular brands of chemicals and equipment named are necessarily the best for the purpose.

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Table 1

Standards for Column Calibration

Compound	Source	Nominal MW Value	M_n [b]	Analytical Data [a] M_w [c]	MWD [d]
Polystyrene	Arro [e]	600	600 ± 7%	-- [f]	1.10
Polystyrene	Arro	800	811 ± 7%	--	--
Polystyrene	Arro	2,100	2,115 ± 7%	--	1.10
Polystyrene	Arro	4,000 [g]	3,110 ± 5%	--	--
Polystyrene	Arro	12,000	12,000	12,200	1.10
Polystyrene	Arro	19,000	18,900	19,400	1.03
Polystyrene	Arro	50,000	50,400	52,100	1.03
Polystyrene	Arro	111,000	111,000	111,000	1.00
Polystyrene	Arro	233,000	217,000 ± 6%	257,000 ± 6%	1.17
Polystyrene	Arro	390,000	383,000	392,000	1.02
Polystyrene	Arro	630,000	632,000	694,000	1.10
Polystyrene	Arro	1,500,000	--	1,500,000	1.10
Polymethyl methacrylate	Poly sci. [h]	75,000	--	--	1.10

[a] All data provided by manufacturer

[b] Number average molecular weight

[c] Weight average molecular weight

[d] Molecular weight dispersion (M_w/M_n)

[e] Arro Labs., Joliet, Illinois

[f] A blank line indicates data not provided

[g] In preparing the calibration curve, our best estimate value of 3100 was substituted for the manufacturer's nominal WM of 4000

[h] Polysciences, Inc., Warrington, Pennsylvania

2.2 Instrumental Methods

The HPLC-UV/RI-GFAA system [11] is outlined schematically in figure 1. A high pressure pump (Altex Model 110A, Berkeley, California), equipped with a single sapphire piston in conjunction with precision inlet and outlet valves, was used to deliver solvent at the controlled flow rate of 1 mL min^{-1} in the present work. Isocratic conditions were employed. Solutions of organometallic compounds, or polymers of standard MW, were injected (50 µL) into the SEC system via an on-line high pressure syringe loading sample injector (Rheodyne Model 7120, Berkeley, California). An in-line precolumn filter, pore size 2 µm (No. 84560, Waters Associates, Milford, Massachusetts) was used to protect columns employed for SEC. The columns were packed with porous, highly cross-linked polystyrene-divinylbenzene (PS-DVB) copolymer (µStyragel, Waters Associates), have a particle size of 10 µm. Columns used for separations were three µStyragel columns in series, nominal pore size 10^3 Å. The µStyragel column dimensions were 300 by 7.8 mm i.d. Columns were connected by 100 mm lengths of 1.5 mm o.d., 0.2 mm i.d. stainless steel tubing, and to a fixed wavelength (λ = 254 nm) RI/UV dual detector (Knauer, Utopia Instruments, Inc., Joliet, Illinois). 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 detector cell outlet to a specially constructed PTFE "well sampler" described previously [12], from which 20 µL aliquots were automatically withdrawn at 55.5 s intervals (Δt). A Perkin-Elmer (Norwalk, Connecticut) Model 360 dual-beam atomic absorption spectrophotometer with deuterium lamp background corrector and Model HGA 2100 graphite furnace atomizer (GFAA) were used for specific element detection. GFAA program: λ, 224.6 nm; drying time, 10 s, 100 °C; charring time, 10 s, 200 °C; atomization time, 10 s, 2700 °C; atomization interval, 55.5 s. In
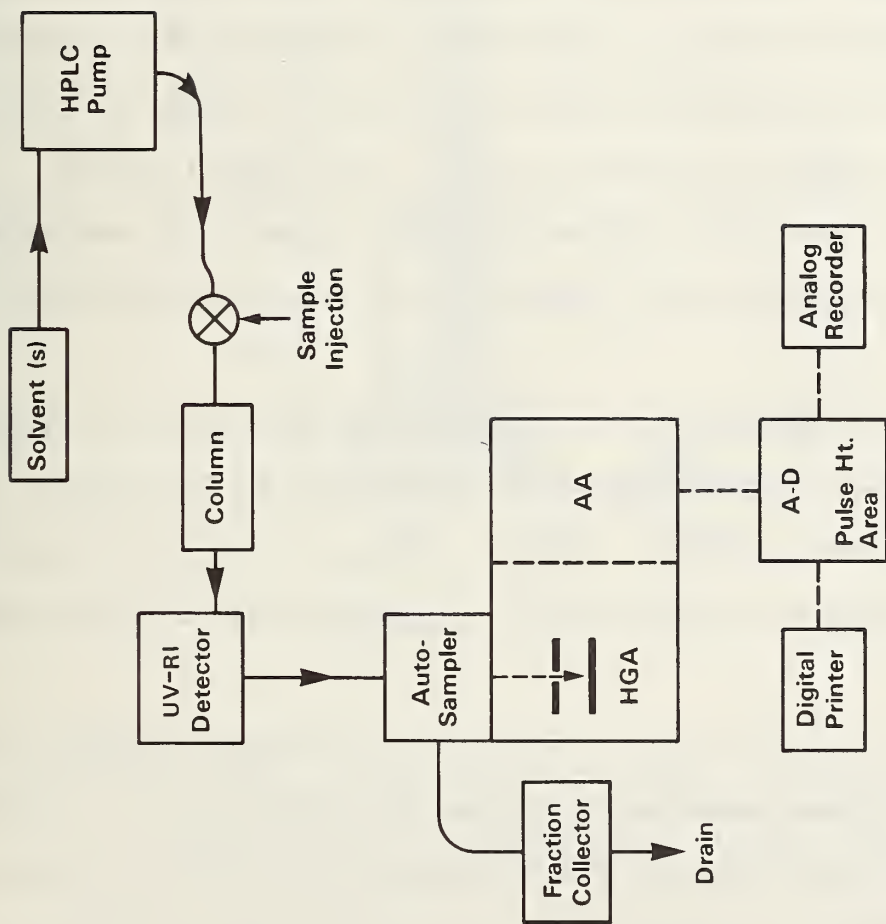
Figure 1. Block diagram summarizing the SEC-UV/RI-GFAA system, including accessory devices. In the present experiments, the auto sampler continuously aliquoted 20 µL specimens into the graphite furnace at intervals of 55.5 s [11].

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GFAA chromatograms, the observed peak heights represent measured absorbances due to the quantities of an element contained in a 20 μL aliquot introduced into the furnace and volatilized at 2700 °C. Only about 2 percent of the total effluent is volatilized at a flow rate of one mL min^{-1}. An automatic digital integrator (Infotronics Model CRS-204, Infotronics Corp., Austin, Texas) was used to obtain a digital record of AA absorption intensities.

A Waters Model R401 differential refractive index indicator was used to obtain the ΔRI data from which was prepared the histogram of OMP-1, shown in figure 2. The sample was dissolved (1/100 w/v) in THF and injected (300 μL) into a system consisting of four SEC columns in series: two μStyragel columns having nominal pore size of 10^3 Å, and two μStyragel columns having nominal pore size of 10^2 Å. The column dimensions, the connectors, and flow rate were as described above.

Eluent was collected during this entire chromatographic run in either 0.5 mL or 1.0 mL segments for subsequent off-line analysis for tin by GFAA, in order to plot the intensities of GFAA tin signals obtained from 20 μL aliquots of the consecutive fractions and compare their intensities with those of corresponding ΔRI signals.

SEC column calibration was performed with polystyrene standards, having a molecular weight range encompassing that of observed OMP fractions. A calibration curve is illustrated in figure 3 and is presented on the scale of elution volume (V_R') in figure 4.
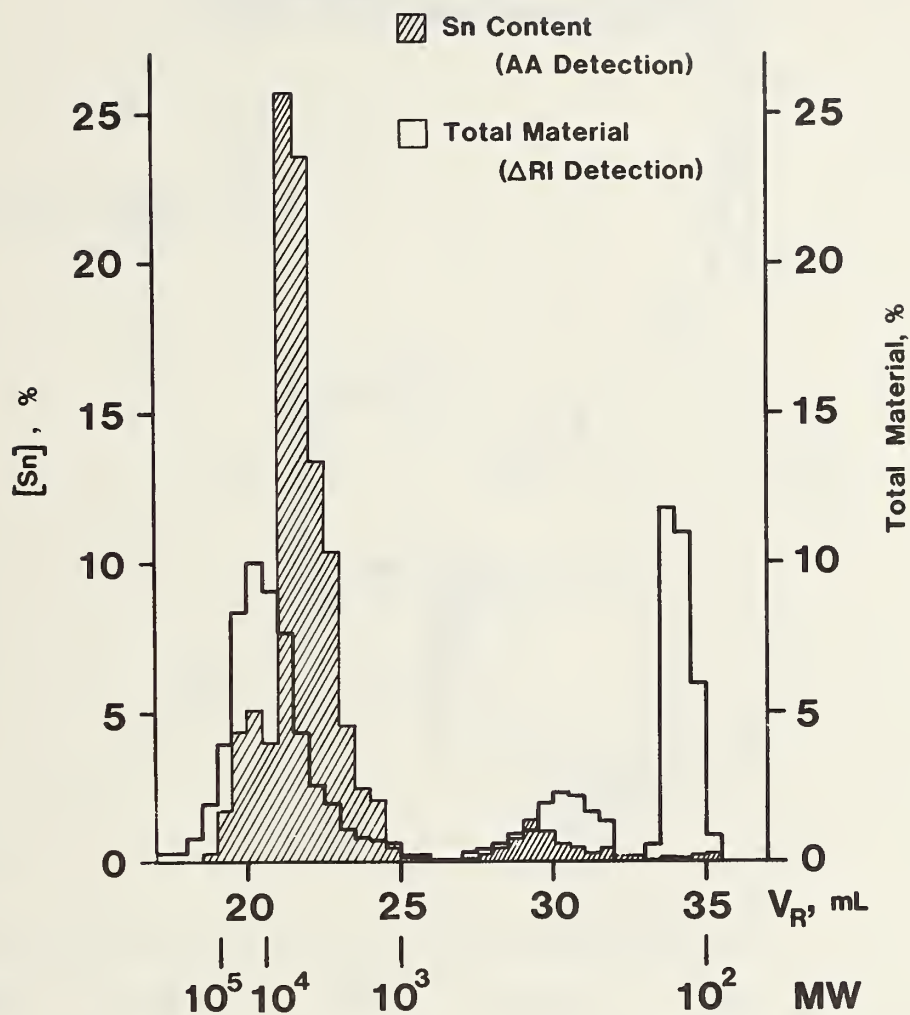
OMP-1

Figure 2. SEC-RI-GFAA chromatogram of OMP-1, a terpolymer of methyl methacrylate, tributyltin methacrylate, and tripropyltin methacrylate. Solvent, THF. Columns: Waters μStyragel (four) in series; two of average pore size 10^3 Å and two of average pore size 10^2 Å. Mobile phase, THF. Flow rate, 1.0 mL min^{-1}. RI detector, Waters Model R-401. Injected volume, 300 μL. Injected concentration of polymer, 3.0 mg/300μL. Fractions were collected for off-line determination of tin by tin-specific GFAA. Each peak in the respective histograms represents a percentage of the total amount of detected tin (GFAA) or detected materials (ΔRI).
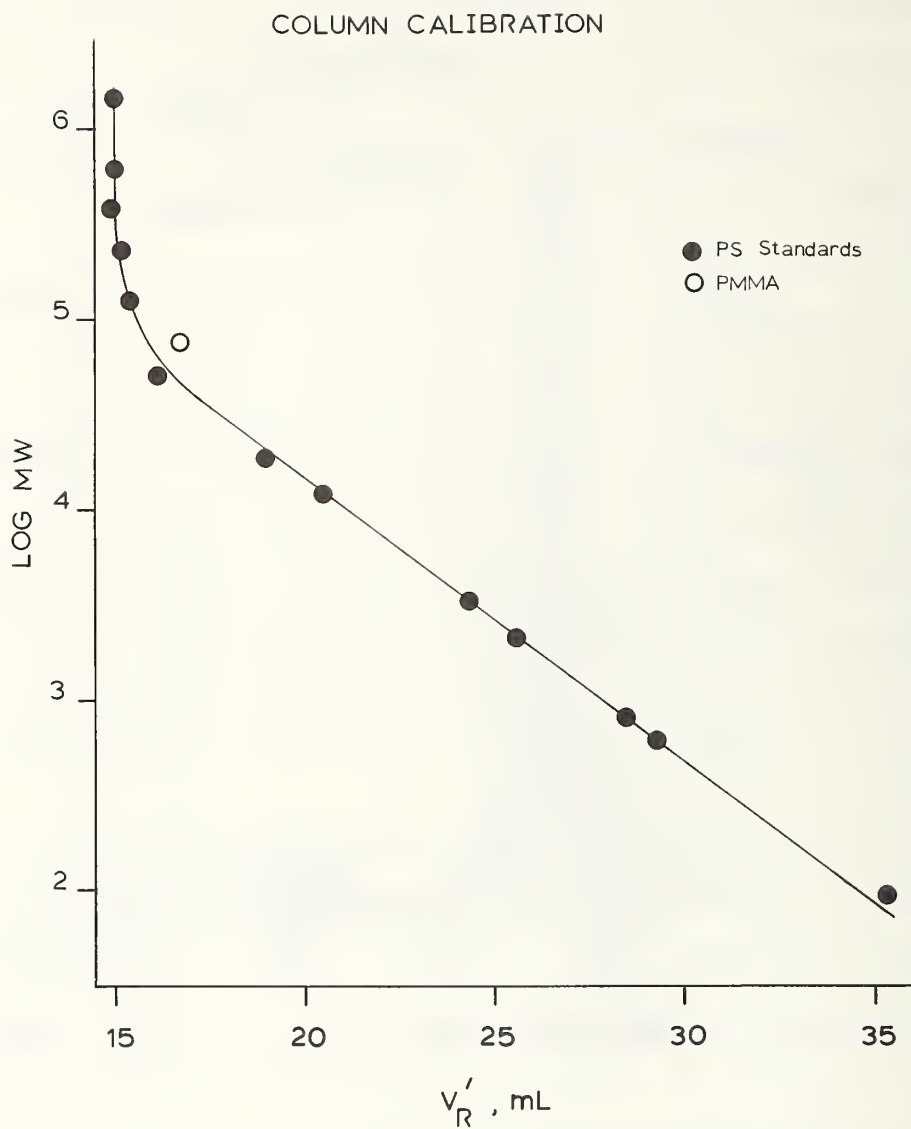
COLUMN CALIBRATION

Figure 3. Column calibration based on elution volumes of PS and
toluene. Each point represents the intersection of tangents
extrapolated from straight line portions of the respective
chromatographic absorption spectra of polystyrene standards
listed in table 1. V_R' represents retention volume corrected
for 0.1 mL of dead volume between the column and the UV/RI
detector. The point for PMMA (open oval) was omitted in
calculating slope and correlation coefficient (0.997) of
the plot of log MW vs V_R'.

SEC - UV - GFAA CHROMATOGRAMS OF TBTM - MMA COPOLYMERS INITIATED BY CONCENTRATIONS OF BENZOYL PEROXIDE INCREMENTED LOGARITHMICALLY

I = 0.03

UV

AA

AA

UV

I = 0.10

UV

UV

AA

I = 0.30

UV

AA

I = 1.00

MW 10^5 10^4 10^3 10^2

20   40
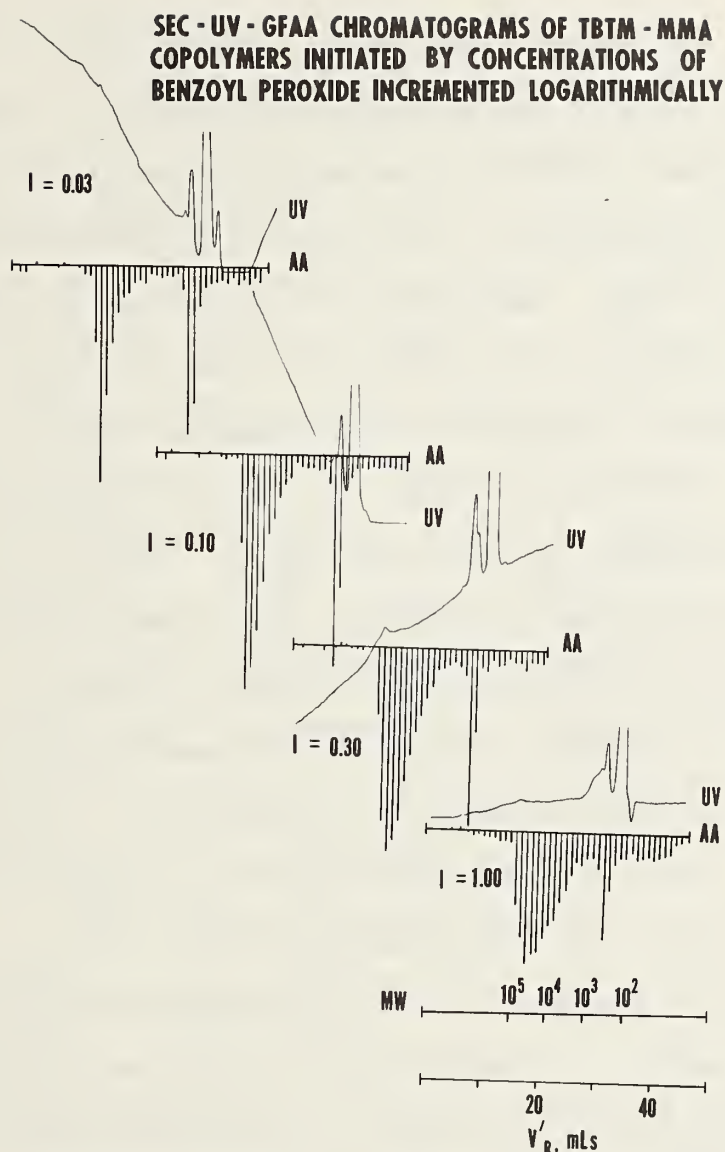V'_R, mLs

Figure 4. SEC-RI-GFAA chromatograms of TBTM-MMA copolymers reacted
           for 24 h in refluxing benzene (80.1 °C) in the presence
           of concentrations of benzoyl peroxide incremented in
           logarithmic steps.

2.2.1   Nuclear Magnetic Resonance

          All NMR spectra were run on a CXP-200 NMR spectrometer (Bruker

Instruments Inc., Billerica, Massachusetts), equipped with a tunable broad band

probe, at a field strength of 4.7 T.   All spectra were run in 20 mm o.d. spinning

sample tubes.   Tin-119 spectra (74.6 MHz) were run on a 10 percent w/v solution

of polymer in THF.   The spectral width was typically 36 ppm using a 35 µs pulse

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(90° flip angle). The number of data points was 8192 (8 K), and a 6 Hz line broadening function was used before Fourier transformation. Since preliminary experiments showed the field drift to be negligible compared to the width of the Sn lines, the spectrometer was run unlocked. Decoupled spectra were run in the nOe suppressed mode. Maximum acquisition time was not over 20 min. All chemical shifts are reported with reference to external $(CH_3)_4Sn$ as zero, with shifts to high frequency (downfield) of the resonance reported as positive [13]. Carbon-13 spectra (50.3 MHz) of polymer were run on a 20 percent w/v solution in benzene containing about 10 percent benzene-d_6. TBTO was run as a neat liquid containing five percent $(CD_3)_2CO$ as a lock. The spectral width was chosen according to the spectral region (aliphatic, carbonyl, or total) that was to be viewed. A tailored pulse sequence was used to minimize the interference from the high concentration of benzene [14]. The number of data points taken was either 8 K or 4 K, with zero fill, if needed, to improve interpolation on peaks. Line broadening was used according to the particular signal it was desired to emphasize. The spectrometer was locked to the deuterium signal of the benzene-d_6. All spectra were run with proton decoupling, using the two level sequence to preserve nOe with minimum sample heating. Acquisition time varied from less than one hour for the aliphatic region to overnight (14 h) for the carbonyl region. All chemical shifts are reported with respect to benzene taken as 128.0 ppm.

2.3 Experiments

In this section we describe first kinetic studies of copolymerization, then the results of a series of copolymerizations conducted under varied conditions, and finally the treatment of data obtained from the experiments.

2.3.1   Kinetic Runs

For the kinetic runs, TBTM was commercially prepared from high-purity bis(tributyltin) oxide (TBTO) and methacrylic acid. The monomer was recrystallized from petroleum ether at -15 °C to obtain a product claimed by the manufacturer to be typically 98 percent pure after recrystallization. Decomposition of this product was inhibited by addition of 100 ppm of p-methoxyphenol. The product was stored at 4 °C until used. Methyl methacrylate, commercially prepared and inhibited with 25 ppm of p-hydroquinone was used as received. With benzene as the copolymerization medium, a solvent-to-polymer ratio of 2:1 by weight was determined to be optimum. Commercial benzoyl peroxide (1 percent by weight based on the sum of TBTM and MMA) was employed as the initiator. The tetrahydrofuran (THF) used as the solvent for aliquots of sample, contained butylated hydroxytoluene preservative and was purified by filtration before use, employing an organic clarification kit equipped with filters of 0.5 μm pore size.

TBTM (348.8 g, 0.93 mol) and MMA (80 g, 0.8 mol) were added to 857.6 g of benzene in a 2-L, three-neck flask equipped with a thermometer, septum, and condenser. To this mixture was added 4.29 g (0.018 mol) of benzoyl peroxide. The flask and contents were warmed on a heating mantle controlled by a variable transformer at the reflux temperature of benzene (80.1 °C) with continuous magnetic stirring. Ten-mL aliquots were taken from the reaction mixture after preselected periods of reaction (table 2) and diluted immediately to 100 mL with cold THF. The final aliquot in the kinetic series was taken after a 24 h reaction time. These samples were examined by chromatography [11] and by ^{119}Sn FT-NMR.

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Table 2

Fractionation by SEC of Aliquots Taken During Copolymerization of TBTM
and MMA, with GFAA Detection of Tin-Containing Moieties

Aliquot Number	Time of Reaction, min.	Fraction A[a] Integration Counts mV[c]	% Sn	Fraction B[b] Integration Counts mV[c]	% Sn
1	0[d]	19,670	21.1	73,540	78.9
2	0[e]	19,430	17.8	89,730	82.2
3	30	53,240	40.1	79,660	59.9
		34,490	41.3	48,990	58.7
4	60	43,070	53.2	37,900	46.8
5	180	142,000	59.2	97,810	40.8
		65,000	58.0	47,050	42.0
6	360	120,420	64.1	67,510	35.9
7	726	123,840	61.1	78,950	38.9
8	1440	94,850	67.3	46,030	32.7
9	AFTER[f]	145,620	86.5	22,700	13.5

[a]Fraction A = MW 200,000-1,000 daltons

[b]Fraction B = MW 500-100 daltons

[c]Summation of counts

[d]0 = Aliquot taken prior to heating

[e]0 = Aliquot taken at the time at which refluxing began

[f]Aliquot taken after replacement of refluxing benzene by refluxing Stoddard
solvent, involving increase in temperature to 120 °C

2.3.2 Varied Conditions of Polymerization

2.3.2.1 Samples Initiated by Varied Concentrations of Benzoyl Peroxide

To determine the effect on polymer properties of increasing concentrations of benzoyl peroxide initiator, mixtures were prepared of TBTM (375.5 g, 1 mol) and MMA (100 g, 1 mol) to 950.1 g of benzene. The concentrations of benzoyl peroxide were 0.03 percent (0.141 g, 0.0006 mol), 0.10 percent (0.470 g, 0.002 mol), 0.30 percent (1.410 g, 0.006 mol), and 1.0 percent (4.700 g, 0.0197 mol). The respective batches were subjected to reaction for 24 h. Aliquots of these samples were diluted with THF (10 mL diluted to 100 mL) at 4 °C and then stored at the temperature of dry ice (-80 °C), pending chromatographic analysis by size exclusion chromatography coupled with ultraviolet and graphite furnace atomic absorption spectroscopy detectors (SEC-UV-GFAA).

2.3.2.2 Samples Initated by ABIN

In addition to samples initiated by benzoyl peroxide, two other samples were prepared at 60 °C with the same proportions of TBTM, MMA, and benzene, but including, respectively, 0.03 percent and 0.10 percent (0.001 mol and 0.0029 mol) of azobisisobutyronitrile (ABIN). An attempt to prepare a sample initiated by 1.0 percent (0.029 mol) of ABIN resulted in eruption of the contents of the flask within minutes, possibly as a result of the rapid decomposition of initiator into a large volume of nitrogen gas and free radicals in a viscous solution. A powdery white solid found in the hood surrounding the reaction flask was assumed to be a copolymer formed almost instantly under the reaction conditions. Because results obtained when using lower molar quantities of ABIN were similar to those using the same amount of benzoyl peroxide, an experiment with 0.3 percent of ABIN was omitted.

2.3.2.3 Extended Time of Reaction at a Lower Temperature

A sample of TBTM-MMA copolymer was prepared in the presence of 1.0 percent of benzoyl peroxide at a controlled temperature of 63.3 °C rather than 80 °C, for a period of time extended to 72 h, in order to estimate the effect of the slower decomposition of the initiator into free radicals.

2.3.2.4 Addition of Benzoyl Peroxide in Consecutive Increments

A sample of TBTM and MMA was copolymerized at 80.1 °C in the presence of 0.30 percent increments of benzoyl peroxide added initially, after 24 h, and after 48 h. After 24 h, 48 h, and 72 h, 10 mL aliquots were diluted with cold THF to 100 mL and stored at dry ice temperature pending chromatographic analysis.

2.3.2.5 OMP-1 Polymer

A sample of OMP-1, the terpolymer product of tri-propyltin methacrylate, methyl methacrylate, and tributyltin methacrylate was obtained in approximately 1:1 solution in Stoddard solvent (mineral spirits). The sample was dissolved in THF to provide a solution containing about 1 percent of polymer (w/v) and was examined by chromatographic analysis using a differential refractive index (ΔRI) detector. Collected eluent fractions were subsequently analyzed for tin by off-line atomic absorption spectroscopy.

2.3.2.6 OMP-S

OMP-S, a copolymer of TBTM and MMA , was obtained in a solution of benzene. This was subjected in benzene (final composition 20/100 w/v) to characterization by ^{13}C FT-NMR, for comparison with the ^{13}C FT-NMR spectrum of TBTO as a model compound.

2.3.3 Methods of Data Reduction

Weight average and number average molecular weights (M_w and M_n) were determined from chromatographic GFAA peaks corresponding to individual polymeric fractions by the methods described in detail by Yau, Kirkland, and Bly [15,16]. The intensities of individual tin peaks (h_i), proportional to experimental peak heights, were obtained from the digital integrator record. Molecular weights (M_i) corresponding to each (h_i) value were obtained by comparing the corrected elution volume (V_R') with a corresponding point on the column calibration curve shown in figure 4. The logarithm of the molecular weight of the tin-containing species is assumed for present purposes to be that of the polystyrene standard sample that elutes with a corresponding elution volume. From the (h_i) and (M_i) values, M_w, M_n, and molecular weight dispersions (MWD) are calculated according to the following relationships [15]:

$$M_w = \frac{\displaystyle\sum_{i=1}^{n} (h_i - M_i)}{\displaystyle\sum_{i=1}^{n} h_i} \qquad (2)$$

$$M_n = \frac{\displaystyle\sum_{i=1}^{n} (h_i)}{\displaystyle\sum_{i=1}^{n} (h_i / M_i)} \qquad (3)$$

$$MWD = \frac{M_w}{M_n} \qquad (4)$$

The area of each polymer peak was accurately calculated by summation of the individual tin peaks [12,17,18]. GFAA chromatograms usually were separated into fractions at a V_R' of 30 mL, corresponding to a species

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having a molecular weight of about 500. In certain cases, there appeared to be peak overlap, involving not more than one individual tin signal of relatively low intensity, shared by two polymeric fractions. In these cases, 50 percent of the tin signal was attributed to each fraction in summing up total peak areas.

The percent of tin in each separated fraction was obtained by summing up the total of GFAA tin signals, dividing that quantity into the sum of tin associated with the polymer fraction, then multiplying by 100.

3.   Results and Discussion

3.1 Chromatographic Methods of Analysis

The system shown schematically in figure 1 has been adapted from several experiments conducted in NBS laboratories [7,11,18] for fractionation of OMP formulations with multiple detection on-line. For optimal column performance, over-loading must be avoided [18], and the sensitivity of GFAA detection to nanogram quantitation of molecular tin species [12,19] is admirably suited to problems requiring analysis in trace amounts of numerous individual polymer formulations fractionated by SEC.

One example is the kinetic analysis of TBTM-MMA copolymerization under carefully controlled conditions [7]. Since TBTM is eluted by a volume of eluent THF corresponding to that of the late eluting fraction of typical OMP formulations [11] (figures 5 and 6), fractionation by size demonstrated conversion of the tin-bearing moiety with time of reaction. As shown in figure 7 [7], the chromatographic data of a 24 h kinetic run fit a pseudo first-order equation with a reasonably high coefficient of correlation when the degree of conversion is compared with the logarithm of reaction time. Equally important, we found no evidence of discontinuity in this rate of conversion over the period of
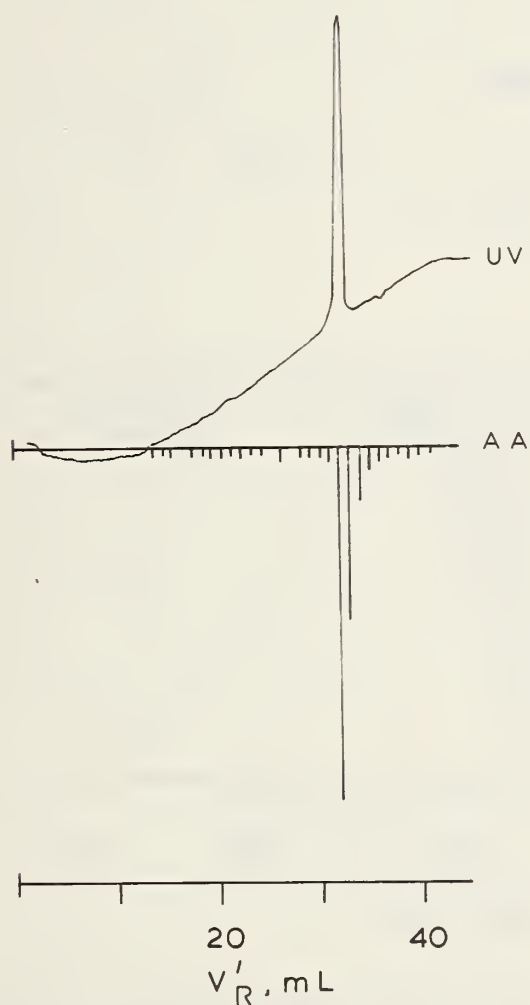
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SEC-UV-GFAA CHROMATOGRAMS OF TBTM

Figure 5. SEC-UV-GFAA chromatogram of tributyltin methacrylate
purified by recrystallization from petroleum ether.
Solvent, THF. Columns: Waters μStyragel (three)
in series; average pore size 10^3 A, mobile phase,
THF. Flow rate, 1.0 mL min^{-1}. UV detector: Knauer
UV/RI Dual Detektor, operating in the UV mode at
254 nm. UV sensitivity, 0.003 AUFS. Injected
volume, 50 μL. Injected concentration of TBTM,
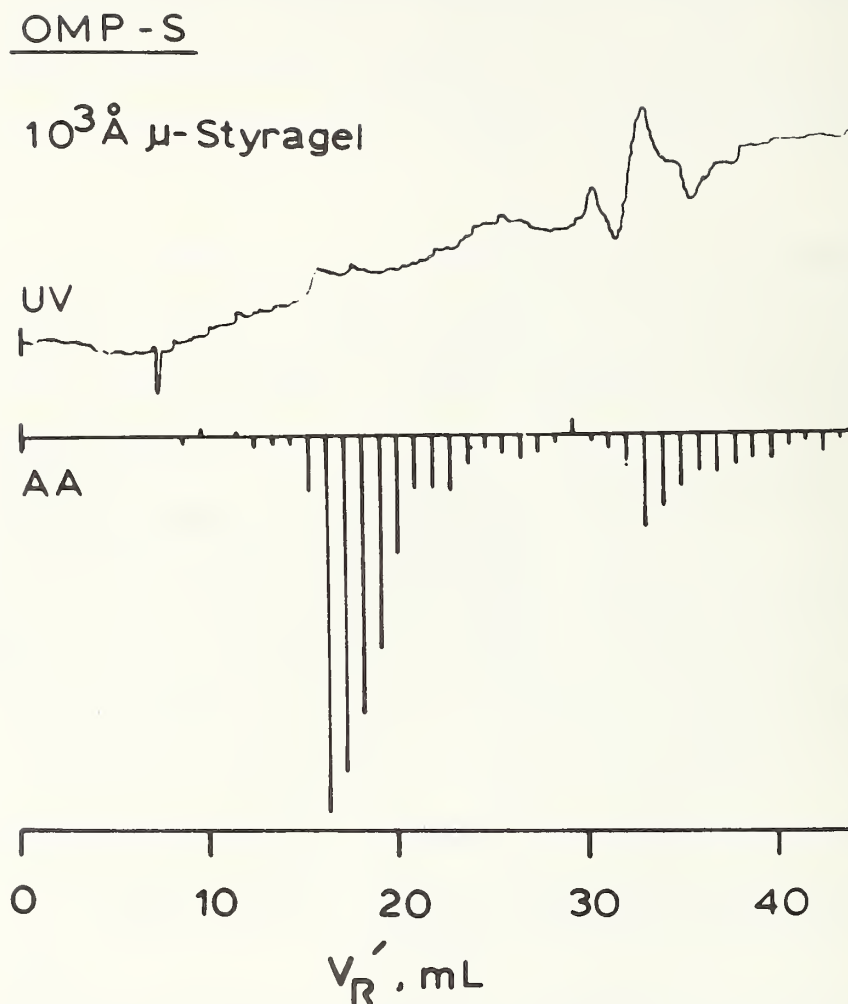50 μg/50μL. GFAA detector, Perkin-Elmer 360.

Figure 6. SEC-UV-GFAA chromatogram of a copolymer of TBTM and MMA. Solvent, THF. Columns: Water μStyragel (three) in series; average pore size 10^3 A, mobile phase, THF. Flow rate, 1.0 mL min^{-1}. UV detector: Knauer UV/RI Dual Detektor, operating in the UV mode at 254 nm. UV sensitivity, 0.003 AUFS. Injected volume, 50 μL. Injected concentration of OMP-S, 25 μg/50 μL.

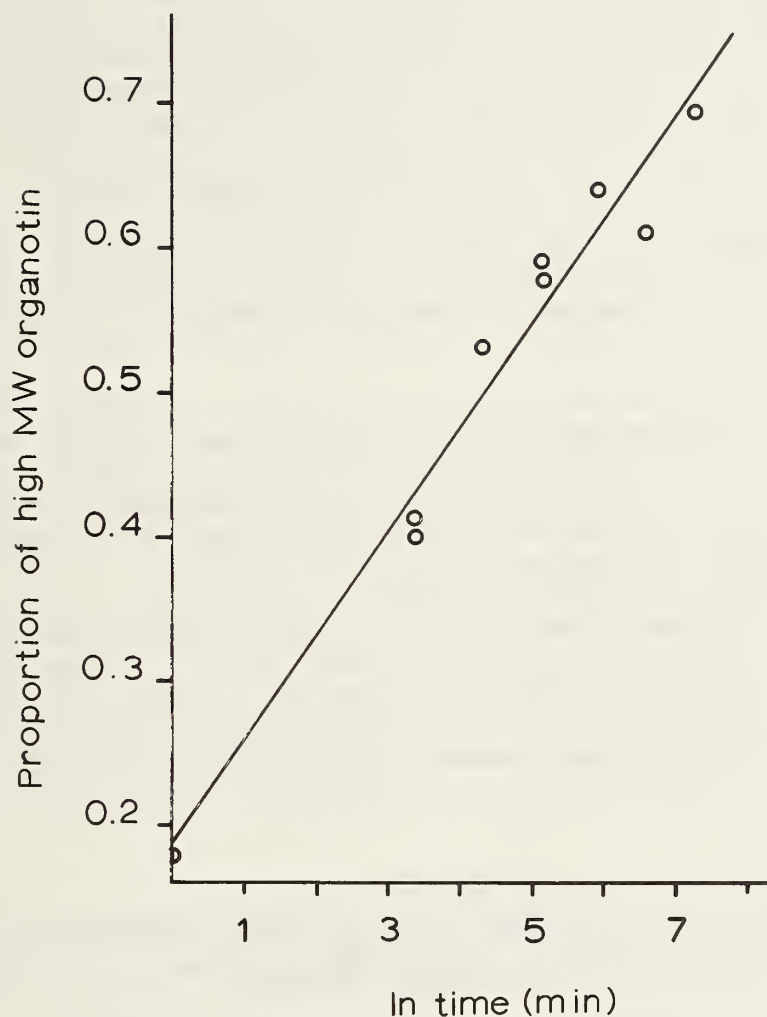## Conversion of TBTM to Copolymer

Figure 7. Increases in high polymer fraction (Δp) plotted as a function of natural logarithm of reaction time ($\ln t$) in minutes, during the free radical copolymerization of TBTM and MMA at 80.1 °C. The observed points fit the equation, $\Delta p = k \, \Delta \ln t + b$, with a linear regression coefficient, $r = 0.978$, $s_r = 0.036$ (7).

reaction time; total conversion, however, of the undesired TBTM fraction would have required a period of reaction of about 30 days, assuming continuity of the conversion process for that period of time.

The molecular weight and the molecular weight dispersion (or narrowness) of the high polymer fraction are important polymer parameters, as

well, and were shown to be essentially independent of the extent of conversion. These facts indicate that polymer chain growth was much more rapid than initiation. Thus, a small number of chains rapidly attained their maximum growth to a molecular weight of about 50,000 daltons. Moreover, as mentioned, molecular size did not exceed 50,000 daltons, even after prolonged reactions, suggesting that mobility, or another physical parameter related to molecular size, determined chain growth and termination in a medium of competitive free radical reactions.

Varying the concentration of benzoyl peroxide initiator resulted, after 24 h of reaction, in the formulations whose chromatograms are exhibited in figure 4. The pertinent data are summarized in table 3.

The MW of the sample initiated with a one percent concentration of benzoyl peroxide is much lower than that of the 24 h aliquot of the kinetic series. Initiator concentrations, monomer concentrations, and chain transfer

Table 3

Effect of Initiator Concentration (Benzoyl Peroxide) on Molecular Characteristics of TBTM-MMA Copolymer

$[I]$ $(\%)^c$	$\ln[I]$	Conversion (%)	MWD^a	M_w^b (daltons)
0.03	-3.506	60.0	1.44	34,600
0.10	-2.303	71.0	2.11	30,800
0.30	-1.204	77.0	2.58	22,300
1.00	0.0	84.0	3.81	15,500
r^d		0.991	0.981	-0.988

[a] $MWD = M_w/M_n$
[b] M_w = weight average mol weight. See Experimental.
[c] $[I]$ = percent initiator by weight of TBTM and MMA in the reaction mixture
[d] Coefficient of linear correlation between $\ln[I]$ and conversion, MWD, and M_w, respectively

agents all affect the MWD of poly(methylmethacrylate) [20]. From the presumed dependence of initiator activity on diffusion control [20], we infer that differences in experimental conditions, such as unequal stirring rates, have a surprisingly large effect on the formation of TBTM-MMA copolymer and will require careful control and evaluation in future copolymerization experiments. The data in table 3, however, do show a striking correlation between the logarithm of the initiator concentrations and corresponding conversion, dispersion, or molecular weight. These data suggest experimental variations to force the reaction to a higher conversion than any obtained in the present experiments, e.g., by incremented increases in stirring rates and/or incremental use of small amounts of initiator, followed by additional quantities, perhaps much larger, over an extended period of time. However, incremental addition of a low concentration (0.03 percent) of benzoyl peroxide under constant conditions resulted in little change in the degree of conversion after the first 24 h (table 4).

At 63 °C, benzoyl peroxide dissociates much less rapidly than at 80 °C. A copolymer initiated by 1.0 percent benzoyl peroxide at 63 °C and allowed to react for 72 h displayed the properties listed in table 4. The MW is much higher than that of the copolymer obtained at 80.1 °C (table 3) in the presence of 1.0 percent benzoyl peroxide but the MWD is nearly the same. The increase in MW shown by this single experiment, together with the relative insensitivity of MWD to temperature, suggests that evaluation of the effect of experimental parameters must include temperature as one of the variables.

It is evident from tables 3 and 4 that azobisisobutryonitrile and benzoyl peroxide initiated reactions yield polymers possessing similar molecular properties, at least for the low concentrations (0.03 and 0.1 percent) of ABIN that have been examined.

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Table 4

Copolymerization of TBTM and MMA Under Various Conditions

Initiator	[I] %	Time (h)	Temp °C	MW[a] (daltons)	MWD[b]	Conversion[e] %
Benzoyl peroxide	0.03	24	80.1	24,800	1.84	67.3
Benzoyl peroxide	0.06[c]	48	80.1	22,900	1.53	70.1
Benzoyl peroxide	0.09[d]	72	80.1	21,300	1.73	66.8
Benxoyl peroxide	1.0	72	63.3	29,250	4.08	75.8
ABIN	0.03	24	60.0	40,900	1.61	61.8
ABIN	0.10	24	60.0	28,000	2.02	73.8

[a]Wt. average MW

[b]M_w/M_n

[c]Increments of 0.03 percent and 0.03 percent w/w added consecutively at 24 h intervals

[d]Increments of 0.03, 0.03, and 0.03 percent added consecutively at 24 h intervals

[e]Conversion based on TBTM with tin-specific detection.

The interpretations discussed so far have all been based on transformations of TBTM only, without recourse to changes in monomeric MMA. The reasons are that the sensitivity of tin detection by GFAA is particularly favorable for evaluating conversion of TBTM, and that TBTM includes the important biocidal moiety that must be incorporated into the polymer, in order for coatings materials actually to work as biocides.

It is experimentally more difficult to follow MMA conversion. The structural similarity to TBTM renders difficult any distinction between the two substances by optical spectroscopy. In figure 2, a GFAA histogram is superimposed on a ΔRI chromatogram of a commercially prepared terpolymer. The low MW peak in the ΔRI chromatogram could be due to both TBTM and MMA; it

is not possible to quantitate the conversion of MMA from this single chromatogram. The relatively small tin peak in the low MW fraction indicates a degree of TBTM conversion equal to or greater than the conversion of MMA. A kinetic run combining SEC-ΔRI chromatograms with superimposed GFAA histograms has not been attempted but would provide a great deal of information on the simultaneous conversion of both tin-bearing and tin-free monomer species.

3.2 FT-NMR

Figure 8 represents the ^{119}Sn FT-NMR spectra of samples selected from the kinetic run illustrated in figure 7. Figure 9 is the ^{119}Sn FT-NMR spectrum of TBTM. Comparison of the two figures demonstrates conclusively that the lower field peak is due to polymer; this increases in intensity at the expense of the high-field peak. The chemical shift of the tin signals appeared to show a quali- tatively large temperature dependence in uncontrolled experiments. A model system, consisting of freshly recrystallized TBTM, was chosen for further experiments. The ^{119}Sn NMR spectrum of TBTM was run at 10° intervals from -20 °C to +10 °C in $CDCl_3$ (locked to solvent) and in THF (locked to added five percent C_6D_6). The ^{119}Sn chemical shift in each solution varied linearly with temperature. A summary of results is given in table 5 and demonstrates that both temperature and solvent effects are indeed large.

Figures 10 and 11 indicate ^{13}C FT-NMR spectra of tributyltin oxide and of a commercial copolymer prepared from TBTM and MMA. Considerable differences arise. Carbon-13 signals appearing near 13, 16, 27, and 28 ppm in the polymer are attributed to the tributyltin residue. There are sharp lines near 19, 125, 135, and 170 ppm, which are probably due to monomer not totally reacted. The two broad signals near 180 ppm are attributed to carbonyl groups in the polymer; one arising from MMA and the other from TBTM. Assign- ment of these lines to their respective monomers awaits examination of comparison

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Table 5

^{119}Sn FT-NMR of TBTM

Solvent	δ^* at 0 °C ppm	$\Delta\delta/\Delta t$ ppm/°C	Linewidth at 0 °C Hz	$\Delta LW/\Delta t$ Hz/°C
$CDCl_3$	110.90	-0.0781	9	0.0
THF	65.25	+0.4748	60	-2.04

$^*(CH_3)_4Sn$ = 0.0 ppm; downfield positive

spectra of PMMA and polymerized TBTM (PTBTM). The interpretation of the methyl region is complicated by the presence of sharp lines, which are probably (at least in part) due to monomers. The complexity of the carbonyl region (near 180 ppm) suggests that monomer units are present with all possible nearest neighbors; i.e., random addition to TBTM or MMA to the end of the growing chain. Confirmation of these preliminary results will await analysis of PMMA of known tacticity, as well as PTBTM prepared under conditions that will allow at least an informed guess as to the tacticity of the product.

The broad tin signal found in THF is characteristic of a system in which the atom observed (i.e., tin) is present in two or more different bonding arrangements that are exchanging at a rate comparable with the NMR time scale of approximately 10^4 s^{-1}. A very rapid exchange would give a sharp signal at a weighted average chemical shift; a very slow exchange would give two or more separately resolved sharp signals. In favorable cases, the kinetics of exchange can be determined by line-width measurements as a function of temperature. In the case of the OMP's, the unsuitability of THF and other solvents of similar intermediate coordinating power, as a solvent for ^{119}Sn NMR measurements, is amply demonstrated.

26

SN - 119 FT - NMR OF POLYMERIZATION REACTION

t = 0

t = 30

t = 180

t = 360

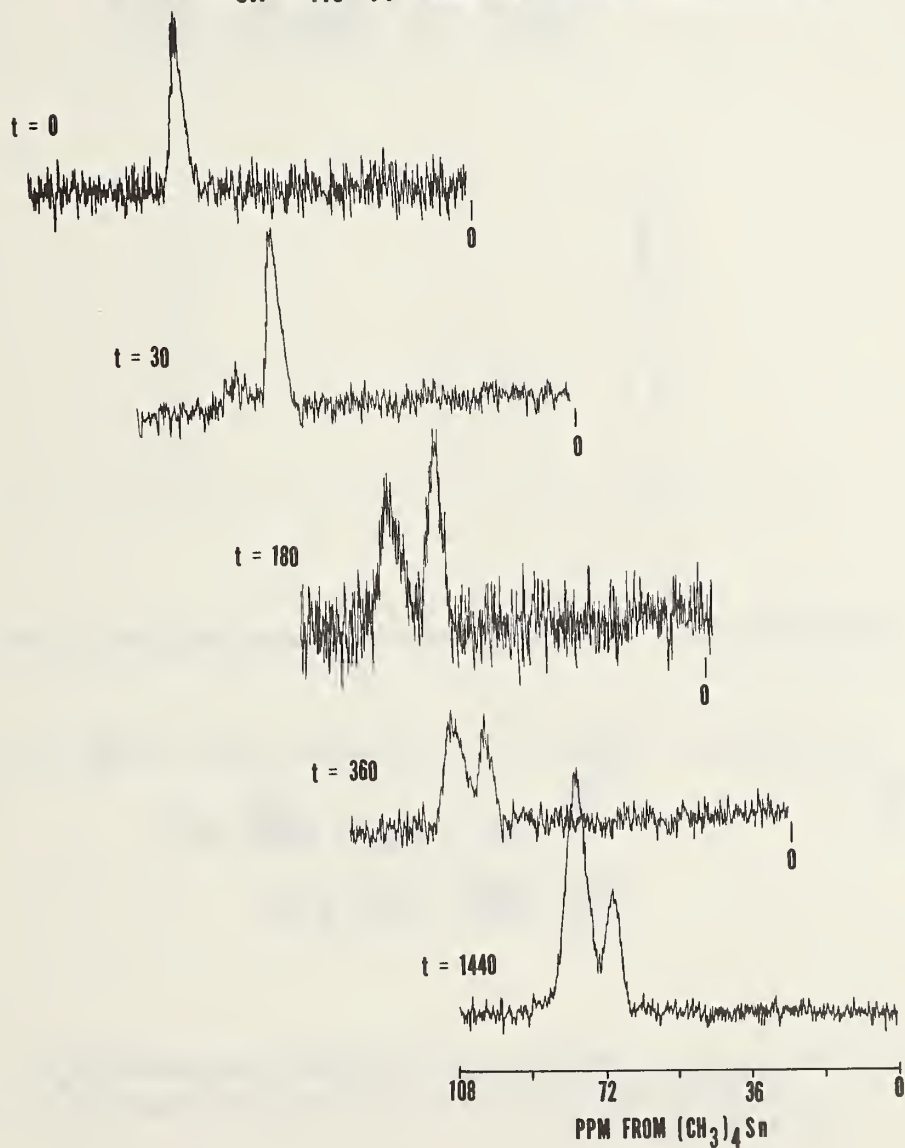t = 1440

108   72   36   0

PPM FROM $(CH_3)_4 Sn$

Figure 8. ^{119}Sn [^1H] FT-NMR spectra of copolymers of TBTM-MMA, following reaction for selected periods of time and showing regular increase in area of signal at lower field, attributed to Sn in polymer. Identical samples were used to obtain data to fit the kinetic equation exemplified in figure 7.
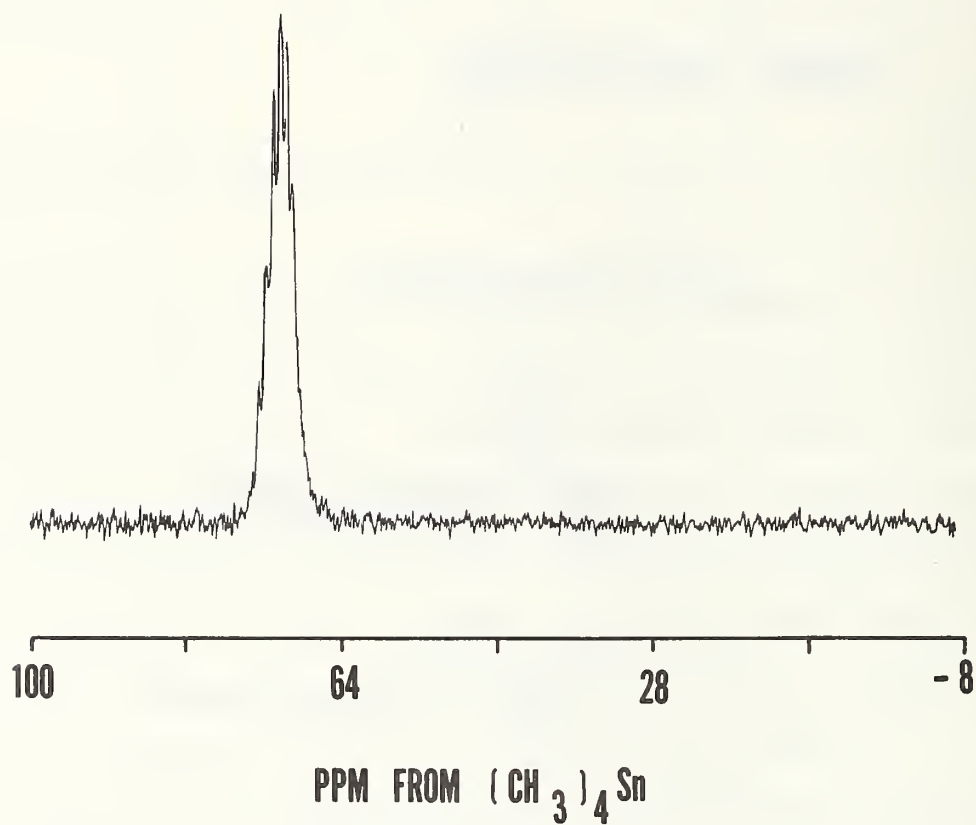
27

SN-119 FT-NMR OF TBTM

PPM FROM $(CH_3)_4 Sn$

Figure 9. ^{119}Sn [^1H] FT-NMR spectrum of TBTM, demonstrating attribution of high field absorbance in figure 8 to unreacted TBTM.
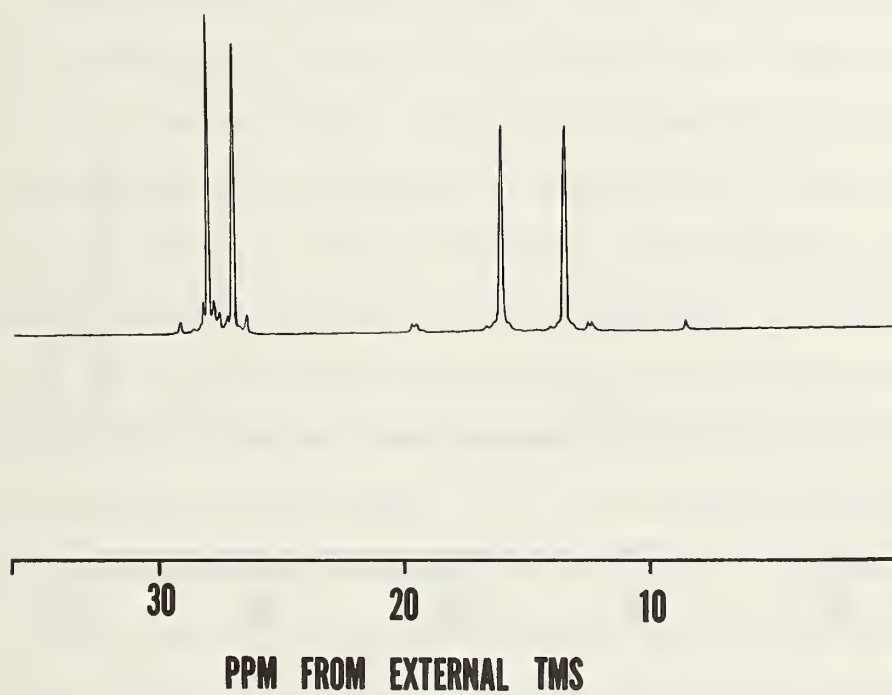
C-13 FT-NMR OF TBTO

PPM FROM EXTERNAL TMS

Figure 10. ^{13}C [^{1}H] FT-NMR spectrum of bis(tributyltin) oxide, $[(CH_3CH_2CH_2CH_2)_3Sn]_2O$

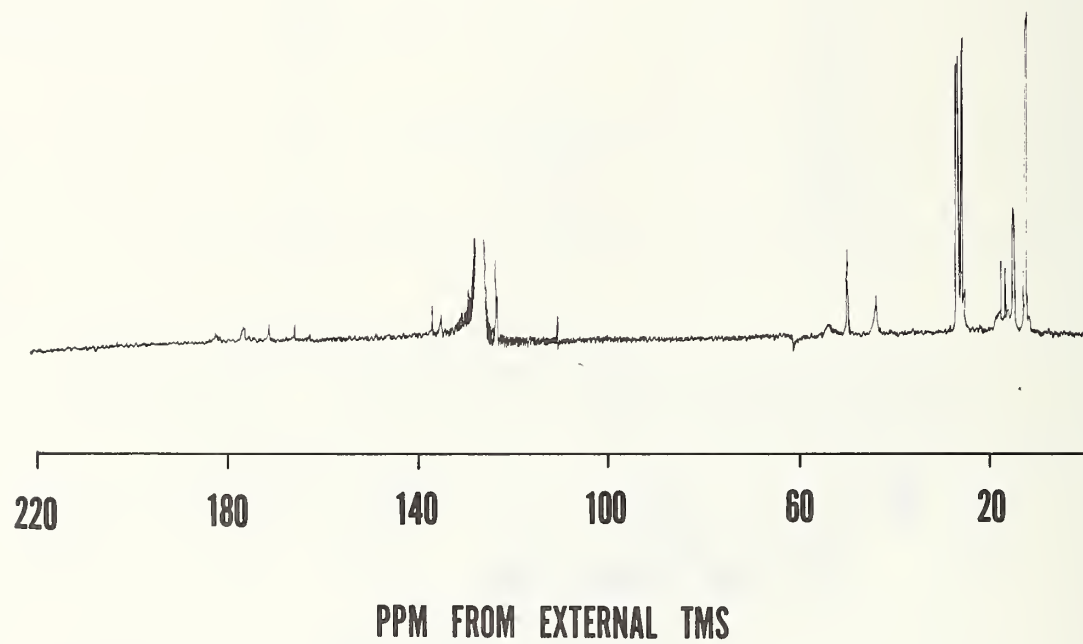# C-13 FT-NMR OF A TBTM-MMA COPOLYMER

PPM FROM EXTERNAL TMS

Figure 11. ^{13}C [^{1}H] FT-NMR spectrum of a copolymer of TBTM and MMA.

Some effort will be spent on finding the most suitable solvent; however, we do not expect to pursue the measurement of exchange kinetics vigorously as a part of this program.

Coupling of a ^{1}H FT-NMR system to an HPLC column has been reported [21,22,23] as an unusual detector which has advantages over the more commonly used detection means in certain special cases. The analysis of a polymerizing mixture of TBTM and MMA may well be one such special case. Proton NMR can unequivocally measure the decrease in signal from protons on doubly-bonded carbons as the polymerization proceeds and thus give kinetic information which does not require pre-calibration of the detector system (inasmuch as proton signal intensities can easily be made directly proportional to proton numbers). The Bureau has a 1.4 T (60 MHz) NMR system which has been converted for FT-NMR; it has been little used since the high field NMR facility was installed and is available for coupling to an HPLC column. It is not known at present whether it will be possible to distinguish between the $=CH_2$ signals from MMA and TBTM at 60 MHz. If this is possible, the additional analytical information it provides will be of great value. Even if only the total signal from $=CH_2$ can be measured, these results can be combined with the analyses for Sn performed by GFAA and the amount of MMA still unreacted can be determined by difference. Accordingly, the construction of an HPLC-FT-NMR system will be pursued in FY82. At the present time, sensitivity considerations limit the proposed system to proton NMR analysis.

3.3 Limitations of Column Calibration with Polystyrene Standards

The assumption underlying SEC column calibration with standard samples of known molecular weight is that retention is size dependent, equally for the standards and unknown whose MW we wish to estimate. This is strictly true only if stereoelectronic interactions between the packing and the respective

eluents are the same. μStyragel (polystyrene cross-linked with divinyl benzene) is not entirely free of surface adsorptivity for polar molecules [24-27] and the validity of MW data based on comparisons between unknowns and standards perforce requires essentially constant experimental conditions. Absolute measurements of MW fractions will require a technique that is directly dependent on size and not on chromatographic retention of MW standards. Low angle laser light scattering technology appears to be one approach capable of determining the molecular weight of chromatographic fractions without recourse to the retention times of standard solutes [28].

The SEC-UV/RI-GFAA work so far reported [7,11,18] has involved analytical scale chromatography. Alternatively, fractional precipitation [29] holds promise for providing the larger quantities of specific polymer fractions required for characterization of configurational sequence by ^{119}Sn FT-NMR and ^{13}C FT-NMR, and absolute identification of low MW species. However, this bulk method lacks the rapidity and convenience of SEC-UV/RI-GFAA for multiple problem solving in synthesis and characterization of OMP's.

3.4 Directions of Future Research

Future research must be designed to provide further information required for writing a Mil Spec which can be met by potential commercial suppliers and which will assure adequate reliability of organotin polymers in use. Analytical SEC-UV/RI-GFAA has identified the research in OMP synthesis and characterization requiring most urgent attention:

3.4.1   Simultaneous determinations of the rates of conversion of the individual types of monomer in the copolymerization of MMA and TBTM. This problem appears to be readily amenable to SEC-RI-GFAA characterization of either an extended kinetic run, such as described already [7], or a series of interrupted runs involving selected monomer compositions [2,3].

3.4.2   Development of a chromatographic technique for performing absolute MW determinations. Because the physico-chemical behavior of standard samples may not be the same as that of unknown polymers, an absolute method is desired. A low angle laser light detector [28] provides the most promising technology available.

3.4.3   Refinement of ^{1}H, ^{13}C, and ^{119}Sn NMR by comparison of experimental spectra with those of known homopolymers in order to measure degree of polymerization in kinetic runs or configurational sequencing in finished polymers.

3.4.4   Correlation of polymer MW with several selected stirring rates, carefully controlled.

3.4.5   Synthesis of model copolymers ultimately providing reference standards for industrial or Mil-spec use.

4.   Acknowledgments

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NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. 81-2424	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

CHARACTERIZATION OF ORGANOMETALLLIC POLYMERS BY CHROMATOGRAPHIC METHODS AND NUCLEAR MAGNETIC RESONANCE

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)

Naval Ship R & D Center
Annapolis Laboratory
Annapolis, MD 21402

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)

Organometallic polymers (OMP) are an increasingly important class of marine surface antifouling agent undergoing intensive development by the U.S. Navy. Candidate OMP's have been characterized at NBS by size exclusion chromatography (SEC) coupled with tin-specific graphite furnace atomic absorption spectroscopy (GFAA) as well as by Fourier transform nuclear magnetic resonance (FT-NMR). The key molecular parameters of many OMP's, the kinetics of formation of a typical copolymer, and the effects of different concentrations of free radical initiators on the formation of a copolymer in a well-stirred reaction system have all been characterized by means of SEC-GFAA chromatograms. FT-NMR spectra of ^{119}Sn have given kinetic information in good agreement with that obtained by SEC-GFAA. Both chemical shift and linewidth of the tin NMR signal have been shown to have an unusually large solvent and temperature dependence. Directions for future research on OMP's are discussed.

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

atomic absorption spectroscopy; biocide; chromatography; copolymers; kinetics; NMR; organometallic polymers; polymers; size exclusion chromatography; slow-release antifoulant; tin.

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USCOMM-DC 6043-P80