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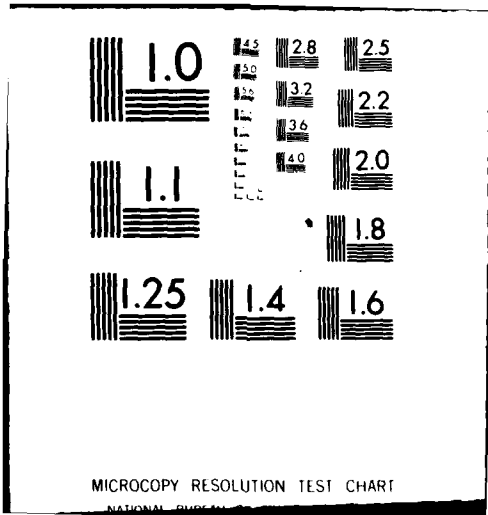
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Characterization by Tin-Specific Size Exclusion Chromatography of the Free Radical Copolymerization of Tributyltin Methacrylate and Methyl Methacrylate

by

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ABSTRACT

Copolymers of tributyltin methacrylate (TBTM) and methyl methacrylate (MMA) comprise an important class of biocidal slow-release organometallic polymers (OMP's). Little is known of the kinetics and mechanism of copolymerization. TBTM and MMA were copolymerized in the presence of a free radical initiator (benzoyl peroxide) at 80.1 °C. Aliquots, taken at preselected intervals from 0 to 1440 min, were fractionated by size exclusion chromatography (SEC) coupled with ultraviolet (UV) and tin-specific graphite furnace atomic absorption (GFAA) detectors. A UV absorbance observed at 254 nm was associated with low molecular weight (MW) species, decreasing in concentration continuously with time of reaction. Tin-specific GFAA indicated a decrease in low MW species (c. 350 daltons) with concurrent increases in high MW species (c. 40,000 daltons). The fraction of high MW increased as a linear function of the logarithm of the time of reaction. SEC-UV-GFAA thus provides a tool of major importance for characterizing the time dependence and continuity of the process by which monomers of TBTM are converted to a useful bioactive slow-release coating material.

KEY WORDS

Copolymerization; fractionation; kinetics; methyl methacrylate; molecular weight dispersion; number average molecular weight; organotin polymer; size exclusion chromatography (SEC); tin-specific graphite furnace atomic absorption (GFAA); tributyltin methacrylate; ultraviolet absorbance; weight average molecular weight.

INTRODUCTION

The free radical copolymerization of triorganotin-substituted, unsaturated esters, such as tributyltin methacrylate (TBTM), with methyl methacrylate (MMA) provides valuable, controlled-release biocidal organotin macromolecules [1]. These candidate organometallic polymers (OMP's) represent a novel class of tailored materials especially effective as long-service marine antifoulants on ships [2]. Prior to the commercial utilization of the polymers, specific information must be obtained regarding the polymerization process. Synthetic work done to date has indicated that minor changes in the reaction procedure can cause widely diversified polymer characteristics.

In order to elucidate the characteristics of polymers with optimal anti-fouling performance, a joint research program was established between the authors' respective agencies. The David Taylor Naval Ship Research and Development Center was assigned the task of defining the specific commercially adaptable procedures for synthesizing reproducible polymers. The National Bureau of Standards developed the analytical techniques to characterize the products of the synthesis, and jointly the authors are attempting to elucidate the reaction mechanism.

We have discussed in earlier papers [3,4] the application of size exclusion chromatography coupled with ultraviolet and graphite furnace atomic absorption spectroscopy (SEC-UV-GFAA) for the analysis of OMP formulations. The highly sensitive GFAA detector demonstrated that OMP's of current interest are resolved into two fractions, having weight average molecular weights (M_w) in the range of 50,000-20,000, and about 350. The fraction of low M_w comprised 10 to 20 percent of the whole amount of tin-containing species.

This amount of low M_w tin-bearing species in the formulation is undesirable because: (1) coatings containing excessive low molecular weight

fractions tend to be very soft and do not exhibit desirable physical wear characteristics in marine exposure, and (2) the low M_w fraction complicates the mechanism and rate of release of the toxic moieties we wish to control. Jewett, for example [5], has discovered a rapid, early release of tin-bearing moieties from OMP's immersed in water. Others found that prolonged slow release from the same OMP followed a zero order mechanism [2] during years of exposure to a marine environment.

In the present research, we have initiated experiments to characterize by SEC-GFAA the time dependence and continuity of the process by which monomers of TBTM are converted into a copolymer with MMA in the presence of a free radical initiator at 80 °C.

EXPERIMENTAL

The SEC-UV-GFAA equipment and system has been described in detail previously [3,6]. The mobile phase, tetrahydrofuran (THF), was delivered at the controlled rate of 1.00 mL min⁻¹, under isocratic conditions. Organometallic compounds, or compounds of standard molecular weight, were injected in solution (50 µL) into the SEC system via an in-line high pressure syringe loading injector. The columns were packed with porous, highly crosslinked polystyrene-divinylbenzene (PS-DVB) copolymer, having a particle size of 10 µm and nominal pore size of 10³ Å. Three columns of dimensions 300 by 7.8 mm ID, were used in series. The UV absorbance of eluent was monitored continuously at a wavelength of 254 nm. The GFAA program used a wavelength of 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. GFAA peak heights (figure 1) represented absorbances due to the quantities of tin in 20 µL aliquots introduced into the furnace and volatilized at 2700 °C. An automatic digital integrator obtained a direct record of AA absorption intensities versus time.

Sample Preparation

TBTM was commercially prepared from high purity tributyltin oxide and methacrylic acid. The monomer was recrystallized from petroleum ether at $-15\text{ }^{\circ}\text{C}$ to obtain a product of 98 percent purity, and inhibited with 100 ppm *p*-methoxyphenol (7). It was stored at $4\text{ }^{\circ}\text{C}$ until used. Methyl methacrylate, commercially prepared and inhibited with 25 ppm of hydroquinone, was used as received. Reagent grade benzene was used as the copolymerization medium. A solvent to polymer ratio of 2:1 by weight was determined to be optimum. Commercial benzoyl peroxide was employed as the initiator. The THF employed as solvent and chromatographic eluent, containing butylated hydroxytoluene inhibitor, was purified by filtration before use, employing an organic clarification kit equipped with filters of $0.5\text{ }\mu\text{m}$ pore size and degassed daily by magnetic stirring under a vacuum at ambient temperature.

TBTM (348.8 g, 0.93 mole) and MMA (80 g, 0.8 mole) were added to 857.6 g of benzene in a 2-liter, 3-neck flask equipped with a thermometer, septum, and condenser. To this mixture was added 4.29 g (.018 mole) of benzoyl peroxide. The flask and contents were warmed on a heating mantle controlled by a variable transformer at the reflux temperature of benzene ($80.1\text{ }^{\circ}\text{C}$), with continuous magnetic stirring.

Ten-mL aliquots were taken from the reaction mixture after preselected periods of reaction (table 1), and diluted immediately to 100 mLs with cold THF. Each THF solution was cooled immediately to $4\text{ }^{\circ}\text{C}$ and kept at that temperature until testing. After taking the final 24 h aliquot, the reaction mixture was subjected to replacement of benzene by Stoddard solvent (mineral spirits), during which the reflux temperature rose to $120\text{ }^{\circ}\text{C}$. Inhibitor was added, and one final 10-mL aliquot was taken and diluted to 100 mL with THF.

Data Reduction

The area of each peak in the GFAA chromatograms was calculated by summation of the recorded intensities of the individual tin-specific GFAA peaks [6,8] that may be seen in figure 1. Apparent molecular weights (MW) were assigned to each tin peak as a function of retention volume (V'_R), by comparison with a calibration curve assembled from the V'_R of polystyrene standards.

In the absence of a method for absolute molecular weight determinations, the molecular weight values listed in table 2 are proffered as an internal scale to indicate the progress of the copolymerization. Such molecular weight assignments are strictly valid only if stereoelectronic interactions between the packing and the respective eluents are the same. It is not meant to imply that polystyrene standards constitute a perfectly satisfactory model for copolymers of MMA and TBTM.

Calibration of the SEC system was performed with polystyrene standard samples of known MW and narrow MW distribution [3,9]. Aliquots are designated in each table according to the time at which they were taken. One aliquot was taken for analysis immediately after adding the polymerization ingredients together and is designated 0. A second aliquot was taken as soon as the mixture had reached the reflux temperature of benzene and is designated 0'. Changes in the polymer fraction, listed in table 1, and plotted in figure 2, are obtained by subtracting the polymer fraction found in aliquot 0 from polymer fractions found in each succeeding aliquot.

Weight average- and number average-molecular weights (M_w and M_n) were determined for the GFAA chromatographic peaks by methods described in detail by Yau, Kirkland, and Bly [10]. The areas of UV peaks of interest were determined with a digital planimeter. UV peak baselines were estimated by drawing a straight line between baselines observed before and after UV activity in the respective UV chromatograms.

DISCUSSION

There is little published information on the mechanism or kinetics of the copolymerization of MMA and TBTM. Deb and Samui [11] studied the rate of homopolymerization of liquid TBTM at 60 °C in a sealed ampoule and found the rate to be a linear function of initiator concentration azobisisobutyronitrile (ABIN) over a limited concentration range, but they have not reported similar research on the copolymerization of TBTM and MMA. Ghanem, et al. [12] initiated studies of the copolymerization of TBTM and MMA in evacuated sealed tubes at 60 °C, using ABIN as initiator. They found the conversion to be nearly ideal, with an azeotropic composition of 50 mol % TBTM and 50 mol % MMA. The reported reactivity ratios were 0.79 for TBTM and 1.00 for MMA.

For the copolymerization of styrene and methyl methacrylate, Mayo and Lewis [13] developed the theoretical relationship

$$\frac{d[S]}{d[M]} = \frac{[S]}{[M]} \times \frac{\sigma[S] + [M]}{\mu[M] + [S]} \quad (1)$$

where [S] and [M] are the molar concentrations of unreacted styrene and MMA, respectively, and σ and μ are the respective coefficients of reactivity. Substituting TBTM monomeric concentration ([T]) for that of styrene in equation 1 and using Ghanem's values for the reactivity ratios, we obtain the relationship:

$$\frac{d[T]}{d[M]} = \frac{[T]}{[M]} \times \frac{0.79 [T] + [M]}{1.00 [M] + [T]} \quad (2)$$

Thus, for our initial concentrations of TBTM and MMA, we find:

$$\frac{d[T]}{d[M]} = \frac{0.93}{0.80} \times \frac{0.79 \times 0.93 + 0.80}{1.00 \times 0.80 + 0.93} = 1.03 \quad (3)$$

From equation (3) one would expect the rate of addition of TBTM to the polymer initially to be somewhat greater than that of MMA, decreasing with consumption of excess TBTM to the azeotropic ratio.

Using tin-specific GFAA to follow the conversion of TBTM to polymer, the rate of increase in tin signal associated with a high polymer fraction [P] should be a direct function of the diminution of TBTM during a period of time, Δt . It is not known, a priori, whether or not $\Delta[T]$ or $\Delta[P]$ is a linear function of Δt . We define "t" as the amount of time required to convert a given fraction of unreacted monomer $[T]_t$ to polymer $[P]_t$. If $([T]_t + [P]_t)$ is normalized, $([T]_t + [P]_t) = 1$ for any GFAA chromatogram in the kinetic series. After the final interval, $[T]_{t\infty} = 0$ and $[P]_{t\infty} = 1$. If ΔP is a linear function of Δt , then the following relationship over the actual progress of the copolymerization will be essentially linear:

$$\frac{\Delta t}{t} = \frac{\Delta P}{[P]_t + [T]_t} = \frac{\Delta P}{1} \quad (4)$$

or

$$\Delta p = k \Delta \ln t + b$$

The raw data obtained after four selected reaction periods are presented as SEC-UV-GFAA chromatograms in figure 1. Normalizing the summated tin signals associated with high and low MW species obviates effects of differences in concentration between aliquots. Plotting $\ln t$ (min) against the fraction of polymer observed after various periods of reaction gives the predicted straight line relationship indicated in figure 2. The raw data are tabulated in table 1. The presence of a high MW species, even before reaction nominally is begun, probably is due to a limited homopolymerization of TBTM on storage, a matter of practical significance that will be tested in future SEC-GFAA studies. Table 2 shows that the weight average molecular weights are in the range of

30,000 to 50,000, regardless of the extent of conversion. Assuming that Ghanem's reactivity ratios (12) continue to hold under reaction conditions of higher temperature and in the presence of a different initiator, then the ratio of TBTM to MMA in our polymers should be approximately 1:1.

With a tin-specific GFAA detector, we follow the conversion of TBTM only, not that of MMA. The high coefficient of correlation (figure 2) between changes in the logarithm of reaction time and the extent of conversion of low MW species demonstrates regular, continuous conversion of TBTM to a polymer. The rate of conversion indicated in figure 2 would require extremely long periods of reaction ($t > 700$ h) to effect a decrease in the concentration of low MW tin-bearing species in the OMP formulation, from the 30 percent remaining after 24 h of reaction (table 1) to less than 5.0 percent. Replacement of benzene with Stoddard solvent, driving the temperature to 120°, also reduced the residual monomer concentration to 13.5 percent (sample No. 9, table 1), possibly with chain scission causing a lowering of molecular weight (table 2). The present data demonstrate the special utility of tin-specific GFAA for characterizing the effect of variations in experimental conditions--e.g., type and concentration of initiator, and reaction temperature--on the rate and completeness of conversion and the molecular weight and molecular weight distribution of the product.

Methods other than GFAA would be required to follow the conversion of MMA to polymeric species. Interesting changes in the UV chromatograms are seen in figure 1. The peak areas of a UV absorption, displaying an elution volume of about 32 to 34 min, are summarized in table 3. We attribute this absorbance to carbon-to-carbon double bonds conjugated with carbonyls, in both TBTM and MMA. The rate of decrease based on UV peak areas is not as well correlated with the log of reaction time ($r = 0.91$) in equation (4). This may be because

our sampling technique did not succeed in providing exactly the same amount of OMP formulation from one aliquot to the next, or because one chromophoric species is consumed some what more rapidly than the other, thereby distorting the correlation. The second peak, of constant intensity in all four chromatogram, is attributed to benzene. More definitive information especially on low MW fracture will be provided in future separation and analysis of individual fractions on a preparatory rather than the present analytical chromatographic scale.

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Table 1

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)		Fraction B ^(b)	
		Integration counts (microvolt-s) ^(c)	% Sn	Integration counts (microvolt-s) ^(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 \equiv 200,000 - 1,000 Daltons

(b) Fraction B \equiv 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.

Table 2

Characterization by SEC-GFAA of Molecular Weights of Aliquot Fractions:
Number Average-, Weight Average-Molecular Weights,
and Molecular Weight Distribution

Aliquot Number	Fraction A			Fraction B		
	M_w (Daltons)	M_n (Daltons)	MWD*	M_w (Daltons)	M_n (Daltons)	MWD
1	45,600	14,300	3.19	214	96	2.23
2	42,800	10,700	4.00	213	167	1.28
3	52,900	29,900	1.77	217	173	1.25
	37,800	14,400	2.63	160	116	1.38
4	39,700	13,600	2.91	181	128	1.41
5	40,300	12,900	3.11	185	132	1.40
	30,400	7,500	4.05	143	94	1.52
6	41,000	11,100	3.68	236	242	0.98
7	39,000	15,700	2.48	165	127	1.30
8	36,300	9,500	3.83	218	175	1.25
9	26,500	7,700	3.46	253	100	2.53

*Molecular weight distribution MWD = M_w/M_n .

Table 3

Characterization by SEC of Aliquots Taken During Copolymerization of
TBTM and MMA, with Detection of Chromospheres by
UV Absorbance at 254 nm.

Aliquot Number	Time of Reaction (Min)	Area of UV Chromatographic Peak (cm^2) (a)
1	0 ^(b)	11.8
2	0 ^(c)	9.10
3	30 ^(d)	6.35 9.19
4	60 ^(d)	4.94 5.73
5	180 ^(d)	5.52 5.44
6	360	3.14
7	720 ^(d)	4.80 1.21
8	1440	0.97

(a) $V_R \cong 32$ to 34 mLs

(b) Aliquot taken prior to heating

(c) Aliquot taken at the time at which refluxing began

(d) Aliquots taken from two separate polymerization runs.

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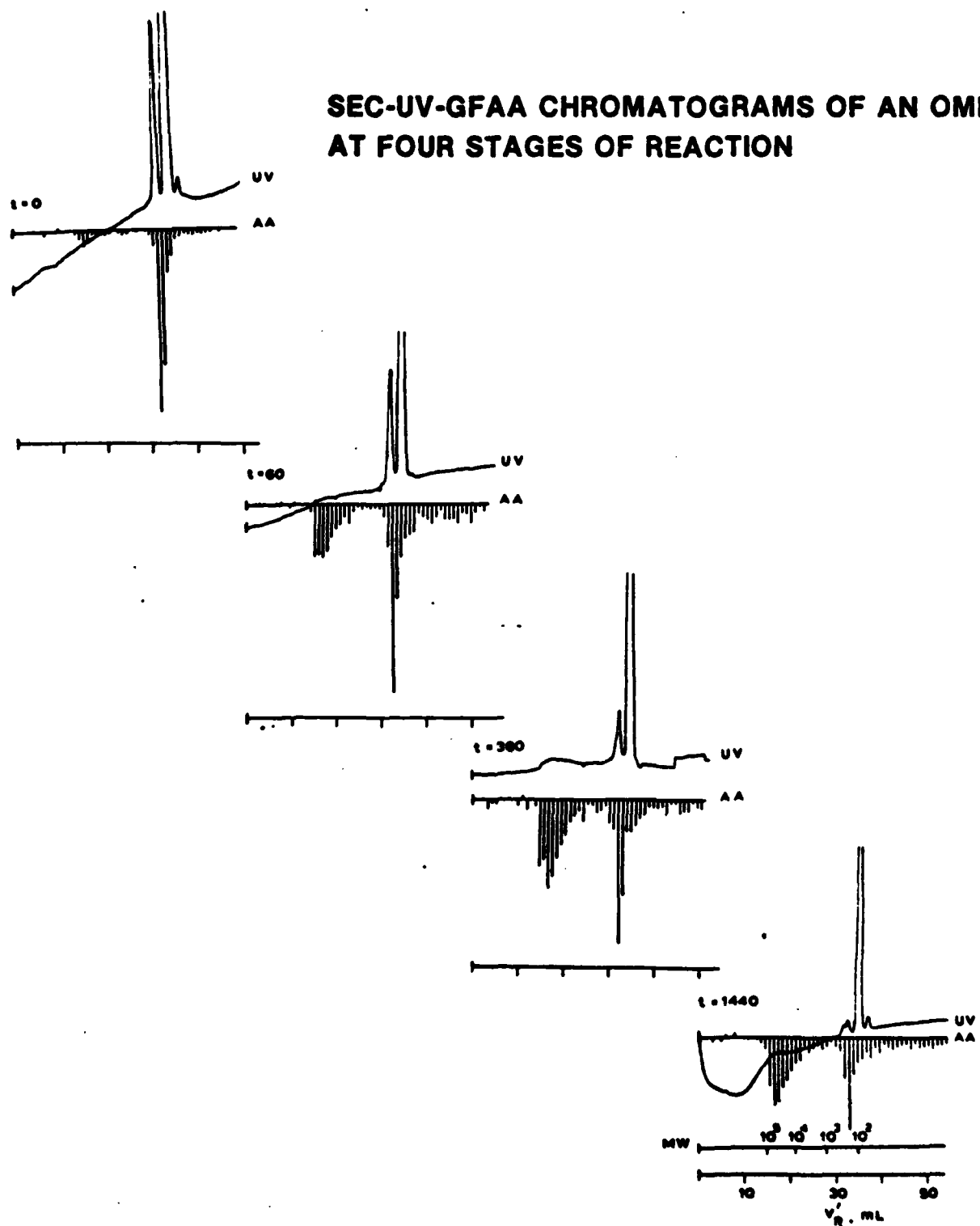
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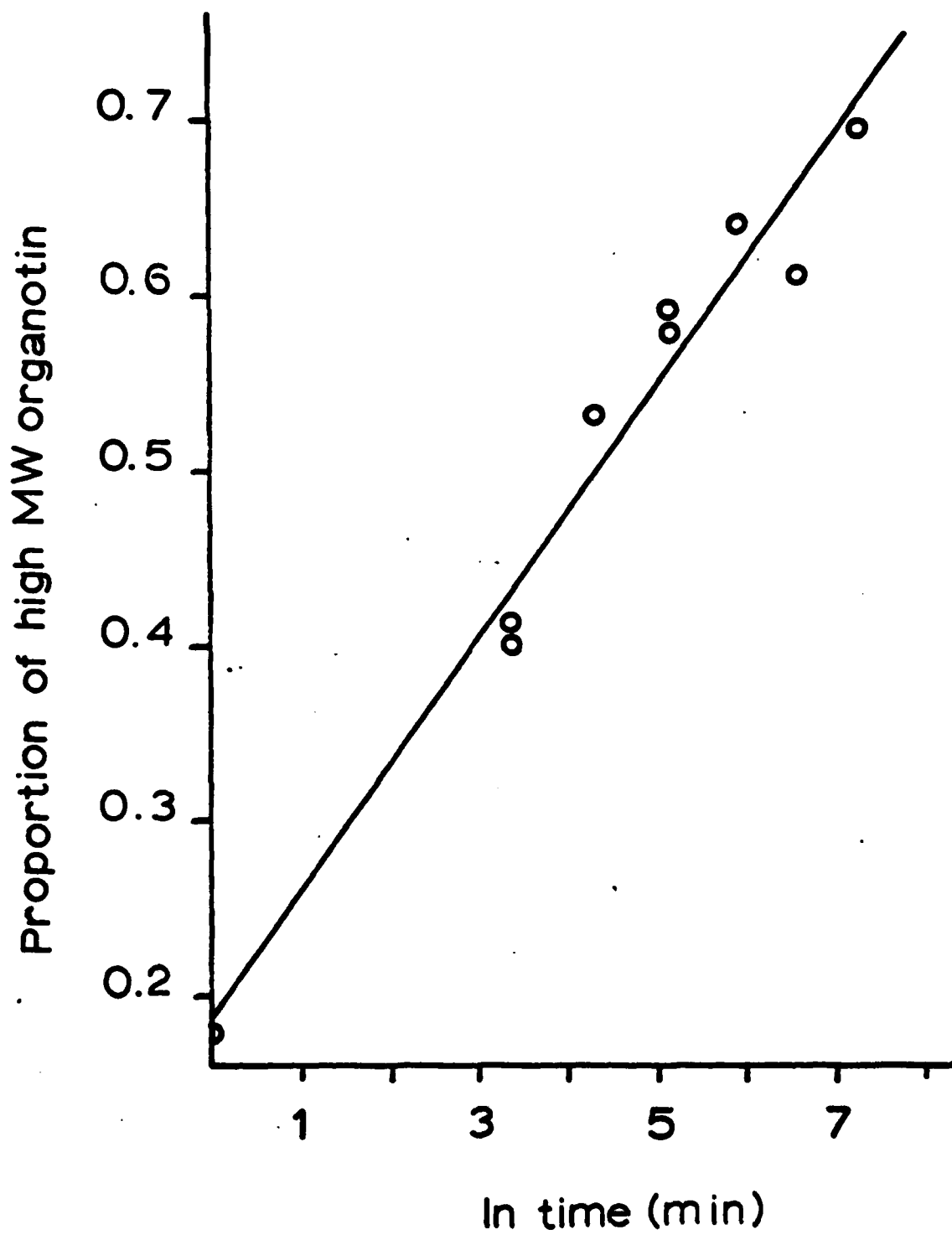
FIGURE CAPTIONS

1. SEC-UV-GFAA chromatograms of aliquots taken during the free radical initiated copolymerization of TBTM and MMA. Solvent, THF. Columns: PS-DVB (three) in series, average pore size 10^3 \AA . Mobile phase THF. Flow rate 1 mL min^{-1} . UV detector operating at 254 nm; UV sensitivity 0.006 AUFS. Injected volume, 50 μL . Injected concentration 50 $\mu\text{g}/50 \mu\text{L}$.
2. Increases in the high polymer fraction plotted as a function of the natural logarithm of reaction time ($\ln t$) in minutes, during the free radical copolymerization of TBTM and MMA at 80.1 $^{\circ}\text{C}$. Slope $k = 0.072$, $s_k = 0.0058$; intercept $b = 0.188$, $s_b = 0.017$; linear regression coefficient $r = 0.978$, $s_r = 0.036$.

SEC-UV-GFAA CHROMATOGRAMS OF AN OMP AT FOUR STAGES OF REACTION



Conversion of TBTM to Copolymer



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20. ABSTRACT

↙ with low molecular weight (MW) species, decreasing in concentration continuously with time of reaction. Tin-specific GFAA indicated a decrease in low MW species (c. 350 daltons) with concurrent increases in high MW species (c. 40,000 daltons). The fraction of high MW increased as a linear function of the logarithm of the time of reaction. SEC-UV-GFAA thus provides a tool of major importance for characterizing the time dependence and continuity of the process by which monomers of TBDM are converted to a useful bioactive slow-release coating material ↘

