

## Radical Copolymerization and Characterization of N-(Tri-*n*-Butyltin) Maleimide Monomer with Styrene, Methyl Methacrylate and N-Vinyl-2-Pyrrolidinone

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Three types of novel organotin copolymers from polymerization of new organotin monomer N-(tri-*n*-butyltin) maleimide with styrene, methylmethacrylate and N-vinyl-2-pyrrolidinone in bulk at 65°C. Using 2,2-azo bis isobutyro nitrile (AIBN) as initiator. Characterization of the prepared copolymers was accomplished by IR, <sup>1</sup>H-NMR spectra and elemental analysis. All the copolymers dissolved readily at room temperature in most polar aprotic solvents. The thermal stability of the polymers was evaluated by TGA and DSC measurements.

### INTRODUCTION

Organotin polymers have been used as pesticides, as wood preservatives and in antifouling paint formulations<sup>1-3</sup>. Maleimide derivatives have been recently advanced as a new vinyl polymer with an excellent thermal stability because of a rigid backbone consisting of a five-membered ring structure. In recent years<sup>4-6</sup>, many organotin polymers have been prepared and applied to a wide variety of fields in which the bioactive groups, SnBu<sub>3</sub> are attached to the backbone of the polymer. In this study, therefore, we carried out radical polymerization of N-(tri-*n*-butyltin) maleimide (N-TBTM) monomer with styrene (ST) methylmethacrylate (MMA) and with N-vinyl-2-pyrrolidinone (N-V2P); all the three copolymers containing N-Sn bond are expected to be used as wood preservatives<sup>1</sup> and protective agents against bacteria and algae<sup>2</sup>.

### EXPERIMENTAL

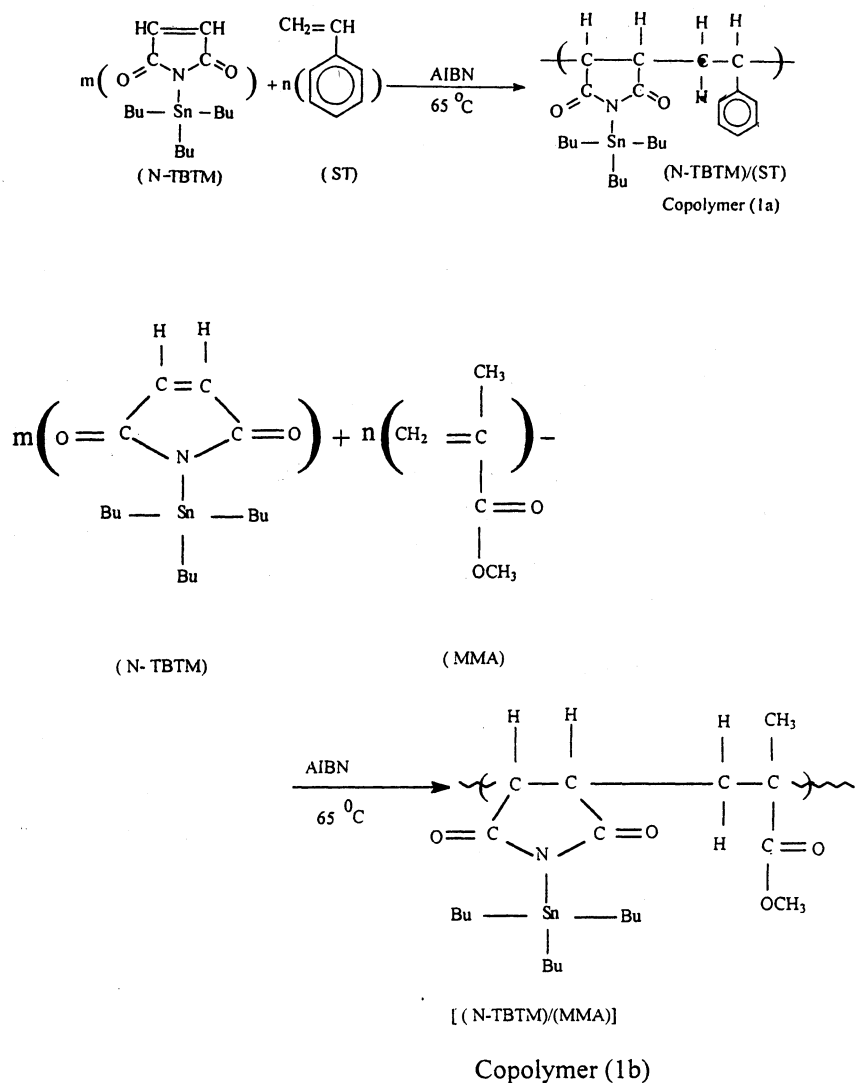
N-(TBTM) monomer was prepared by the reaction of maleimide and Tri-*n*-butyltin oxide (TBTO) in the presence of acetone as solvent<sup>2,7</sup>. ST and MMA were distilled from their commercial materials before use. N-V2P (Aldrich) was used as received; AIBN was recrystallized from methanol, and other reagents were purified by ordinary methods.<sup>8</sup>

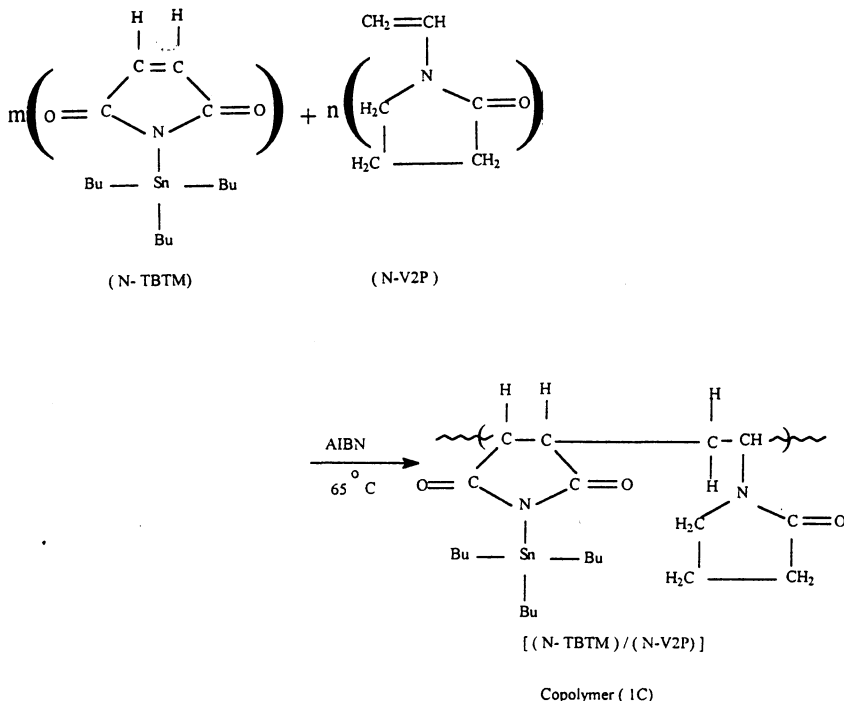
#### Measurements

IR spectra were recorded with a Perkin-Elmer-883 spectrophotometer; <sup>1</sup>H-NMR spectra were recorded on JEOL FX (100 MHz) using TMS as an internal

standard in the indicated solvent having reported  $\delta$  (ppm) values. Molecular weights of copolymers were measured by gel permeation chromatography (GPC) on Waters-150C, equipped with polystyrene gel columns (eluent: tetrahydrofuran). Thermogravimetric analysis (TGA) was carried out in an atmosphere of nitrogen at a heating rate of 10°C/min.

**Polymerization:** Copolymerization was carried out in a sealed glass tube in the presence of AIBN. After polymerization for a given time, the content of the tubes was poured into a large amount of methanol to isolate the copolymers. The copolymers obtained were then washed three times from methanol and dried in vacuum for 24 h to constant weight (Scheme-1).





Scheme 1

## RESULTS AND DISCUSSION

The newly synthesized organotin copolymers of maleimide copolymerized more quickly with AIBN in bulk at 65°C. The average yield of the 3 copolymers was detected by IR and  $^1\text{H-NMR}$  spectra. IR data (obtained in KBr discs) of all these polymers showed the absorption band between 1735–1668  $\text{cm}^{-1}$  for heterocyclic carbonyl vibration. The  $^1\text{H-NMR}$  spectra of all copolymer samples indicate the characteristic proton-NMR shifts. A multiple is observed around  $\delta = 7.07\text{--}7.40$  which may be assigned to aromatic ring protons of styrene a singlet peak at  $\delta = 3.60$  due to a  $-\text{OCH}_3$  group of MMA. The peaks between 0.90–1.58 $\delta$  were due to 27 protons of the TBT moiety and other protons. Gravimetric determination of tin was done as tin oxide<sup>9</sup>. The yields and the average molecular weights of the copolymers, elemental analysis and some physical properties of the copolymers are summarized in Table-1. Qualitative solubilities of the polymers in organic solvents were determined and typical results are listed in Table-2. All three copolymers had good solubilities in polar aprotic solvents such as DMF and DMSO. In concentrated sulfuric acid all the polymers are readily soluble.

TABLE-1  
RESULTS OF ELEMENTAL ANALYSIS AND SOME PHYSICAL PROPERTIES OF  
NOVEL ORGANOTIN COPOLYMERS

Copolymer number	Formula of repeating unit	Unit	% Analysis found (calcd.)				Yield (%)	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
			C	H	N	Sn				
1a	C <sub>24</sub> H <sub>37</sub> NO <sub>2</sub> Sn	490	58.81 (58.78)	7.29 (7.55)	2.35 (2.86)	24.11 (24.29)	53	74400	258200	2.95
1b	C <sub>21</sub> H <sub>37</sub> NO <sub>4</sub> Sn	486	51.66 (51.85)	7.70 (7.61)	2.63 (2.88)	24.73 (24.49)	61	288300	92700	3.11
1c	C <sub>22</sub> H <sub>38</sub> N <sub>2</sub> O <sub>3</sub> Sn	497	53.39 (53.21)	7.41 (7.65)	5.51 (5.63)	24.02 (23.94)	55	(a)	(a)	(a)

(a) Measurement was not possible due to insolubility in THF.

TABLE-2  
SOLUBILITY CHARACTERISTICS OF SYNTHESIZED ORGANOTIN COPOLYMERS

Polymer code	THF	DMF	DMSO	Water	HCOOH	Conc. H <sub>2</sub> SO <sub>4</sub>
1a	+	+	+	-	+	+
1b	+	+	+	-	+	+
1c	-	±	±	-	-	+

(+): Soluble at room temperature.

(±): Partially soluble at room temperature.

(-): Insoluble.

Thermogravimetric analysis and thermal analysis of the prepared copolymers are shown in Fig. 1 and Tables 3 and 4.

TABLE-3  
TGA DATA OF PREPARED NEW ORGANOTIN COPOLYMERS

Copolymer code	Decomposition temperature/°C		T <sub>g</sub> * (°C)	Residue at 800°C %
	T <sub>init</sub>	T <sub>max</sub>		
1a	340	500	102	26
1b	330	380	83	21
1c	330	390	101	34

\*From DSC.

TABLE-4  
THERMAL PROPERTIES OF COPOLYMERS (1a, 1b and 1c)

Copolymer number code	Temperature (°C) for various % decompositions				
	10	20	30	40	50
1a	370	360	395	420	450
1b	320	330	340	345	360
1c	330	350	360	375	430

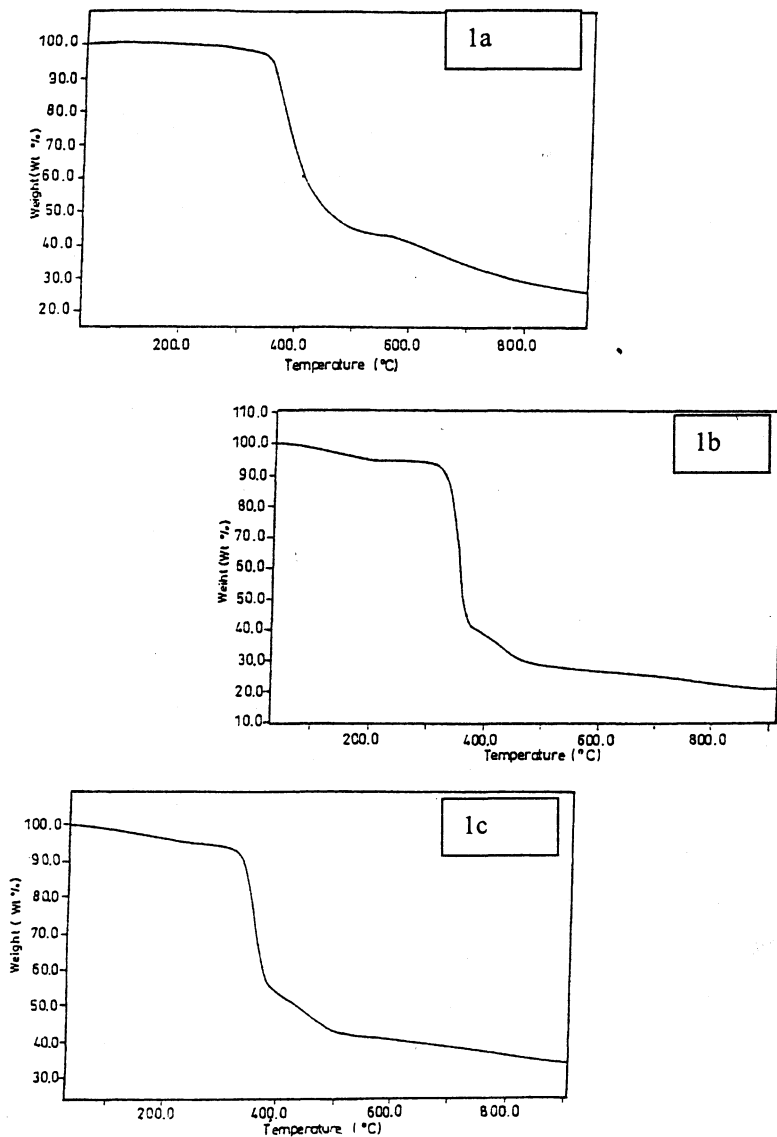


Fig. 1. TGA of 1a, 1b and 1c copolymers

The thermograms of all the three copolymers (1a–c) are shown in Figure 1. Table.3 shows TGA data indicating weight loss at various temperatures. TGA curves show a two stage weight loss. The first stage weight loss was up to 56% for copolymer 1a, up to 53% for copolymer 1b and up to 40% for copolymer 1c and this stage of weight loss seems to be the major degradation step, *i.e.*, slow decomposition, whereas the second stage of decomposition seems to be fast and the weight loss is to be up to 18% for copolymers (1a), up to 14% for copolymer

(1b) and up to 18% for copolymer (1c). Nearly 26%, 21% and 34% residue remained at the end of the reaction for copolymers (1a), (1b) and (1c) respectively; the first stage loss may be due to the degradation of Sn-N linkage which accounts for the maximum weight loss. This view is supported by the temperature of the first stage weight which is up to 330°C, sufficient to break Sn-N linkage. About 6% weight loss of polymers (1b) and (1c) before 100%, possibly due to residual moisture or impurities in the materials<sup>10</sup> on the basis of the initial degradation temperatures and % residue, the thermal stability of the organotin copolymers may be ranked as: 1c > 1a > 1b the copolymer of (N-TBTM)(MMA) were found to be less stable than (1c) and (1a) possibly due to the presence of electron donation methyl groups of methyl methacrylate monomer.

### Conclusion

Three types of N-(tri-*n*-butyltin) maleimide monomer with styrene methyl methacrylate, and N-vinyl-2-pyrrolidone copolymers were synthesized by radical polymerization in bulk at 65°C using (AIBN) as initiator. Polymeric yields were 53, 61 and 55%. Thermogravimetric analysis showed polymer decomposition temperatures (10% weight loss) 330–360°C.

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