

NOTES

Interfacial Preparation and Properties of Poly(tributyltin Acrylate) and Related Polymers

In recent years, much work has been undertaken on organotin polymers, and the materials have been the subject of a detailed review.¹ Solution or emulsion polymerization was originally used to obtain poly(tributyltin acrylate),² but this product may contain impurities due to thermal disproportionation of the organotin groups. The interfacial reaction between trialkyltin chlorides and poly(acrylic acid) should yield a purer product, but a recent investigation³ failed to obtain poly(tributyltin acrylate) by this route. We have successfully prepared poly(tributyltin acrylate), poly(tributyltin methacrylate), and an equimolar copolymer of the two esters by the interfacial method, and here report their molecular weights and glass transition temperatures (T_g) for the first time. An interferometric study of these polymers has recently been reported.⁴

Acrylic acid (5 g) was added to potassium persulfate (0.05 g) in water (125 ml) under nitrogen at 18°C, and the resulting solution was stirred on a water bath at 60–80°C for 6 hr. This solution was diluted with water (375 ml) and neutralized with sodium hydroxide (3 g) in water (50 ml). The solution was then vigorously stirred, using a magnetic stirrer, and tributyltin chloride (24 g) in dichloromethane (500 ml) was added to form an emulsion which was then stirred for 6 hr. After standing 16 hr, the lower layer was separated, filtered, and the filtrate allowed to evaporate leaving a colorless, transparent, tacky, solid polymer (16 g). Due to excessive frothing of the solution, removal of the solvent using a rotary evaporator was not possible. Methanol (6 × 200 ml) was added and allowed to remain in contact with the solid for 24 hr at 18°C each time. The liquid was decanted off and the residue allowed to dry in air at 18°C. A solid polymer (11 g, 60% yield) of poly(tributyltin acrylate), similar to that above and with no pronounced odor of organotin compound, was obtained.

Similar polymers were prepared from tributyltin chloride and poly(methacrylic acid) (55% yield) and a 1:1 mixture of acrylic and methacrylic acids (50% yield).

For comparison, poly(tributyltin acrylate) was also prepared by the thermal polymerization of tributyltin acrylate by heating for 1 hr at 110°C. The polymer was purified by extraction with acetone.

Number-average molecular weights were measured on a Melabs membrane osmometer (CSM2) using an 0–8 S- and S-type membrane at 40°C in toluene solution.

Glass transition temperatures (T_g) were determined on a du Pont Model 900 differential thermal analyzer using the DSC cell. The sample was held in an open aluminum pan and the heating rate was 10°C/min. The properties of organotin polymers prepared by this method are shown in Table I. The calculated values for the elemental analyses are those expected for complete esterification of the carboxyl groups on the polymers by tributyltin groups. The close agreement of the elemental analysis values indicates that a high degree of substitution was achieved.

The molecular weights \bar{M}_n suggest that any low molecular weight material originally present had been removed by the methanol extraction procedure. For comparison, the thermally polymerized sample of poly(tributyltin acrylate) was a viscous liquid with \bar{M}_n of 2.8×10^3 , with appreciable solubility in methanol.

The glass transition temperatures (T_g) of the three polymers (Table I) all fall within a narrow range and may be compared with poly(*n*-butyl acrylate) ($T_g - 55^\circ\text{C}$)⁵ and poly(*n*-butyl methacrylate) ($T_g 15^\circ\text{C}$).⁶ It is suggested that the glass transition is associated with the tributyltin groups.

The infrared spectra of all three tributyltin polymer films showed absorption bands consistent with high-purity, high molecular weight material in contrast to the broad bands previously reported.⁷ In each case, there was a weak carbonyl absorption at 1720 cm^{-1} , and a strong absorption at 1640 cm^{-1} , which is typical of organotin carboxylates in solution,⁸ whereas compounds

TABLE I
Characterization of Organotin Polymers

Polymer ^a	Calculated, %			Found, %			Number Average molecular weight \bar{M}_n	T_g , °C
	C	H	Sn	C	H	Sn		
p-(TBTA)	49.9	8.3	33.0	49.5	8.3	32.4	1.4×10^6	-22
p-(TBT MA)	51.2	8.5	31.7	49.3	8.0	31.8	4.9×10^5	-17
p-(TBTA/MA)	50.5	8.4	32.3	49.7	8.3	32.1	2.0×10^5	-8

^a p-(TBTA): Poly(tributyltin acrylate); p-(TBT MA): poly(tributyltin methacrylate); p-(TBTA/MA): copoly(tributyltin acrylate/methacrylate)-equimolar amounts of acids.

such as crystalline tributyltin acetate showed a chelated carbonyl absorption at about 1570 cm^{-1} , which was absent in the present series. The position of these absorptions suggests that penta-coordinate bridging between adjacent organotin groups is prevented in these three organotin polymers.

All three polymer films had similar absorption characteristics in the ultraviolet region. They were transparent down to 260 nm and showed total absorption by about 230 nm.

Carraher and Piersma³ used a more vigorous stirring rate for a shorter period of time, about 1 min, than the present study, which tended to favor equilibrium conditions with its reaction time of over 6 hr. It therefore appears that tributyltin chloride reacts more slowly with sodium polyacrylate than some of the other organotin chlorides investigated. In the present work, the polymers were all soluble in dichloromethane. This implies that the sodium polyacrylate, originally present in the aqueous phase, reacted with the tributyltin chloride at the interface between the aqueous and dichloromethane solutions and the resulting polymer migrated into the organic phase.

Other trialkyltin chlorides gave lower yields of polymers on reaction under the present conditions. Tripropyltin chloride gave 55% and 50% yields of polymers from sodium polyacrylate and sodium polymethacrylate, respectively, while triethyltin chloride gave yields of 47% and 22% of the corresponding polymers and trimethyltin chloride gave yields of 10% and 22%, respectively. In all these cases, the emulsions produced in the reactions proved very difficult to separate.

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