



Third, such products may offer some useful properties. For instance, tin-containing polyesters of form I exhibit antifungicidal and antibacterial properties. These could be added in small amounts to shirts or clothing to give a product which would be mildew or rot resistant. Also, some of the Group IVA polyesters exhibit moderate thermal stability.<sup>9,10</sup> Thus modified poly(acrylic acids) might exhibit desirable thermal stabilities.

### EXPERIMENTAL

Poly(acrylic acid) was synthesized from freshly distilled acrylic acid. The acrylic acid (150 ml) was added to 200 ml distilled water. To this solution was added 0.1% (by weight)  $\alpha, \alpha'$ -azodiisobutyronitrile. The resulting mixture was flushed with nitrogen to remove oxygen and heated to 65°C. It was maintained at 65°C for 30 min. After an initiation period, the polymerization occurred rapidly and was very exothermic. The resulting solution was dried. The product was purified by washing it several times with water. Further purification was accomplished by dissolving the polymer in water and drying it, thus allowing unreacted acrylic acid to be removed.

The poly(acrylic acid) exhibited a limiting viscosity number of 7.2 (dl/g), which corresponds to a weight-average molecular weight of  $1.9 \times 10^6$  by light-scattering photometry.

The modification of poly(acrylic acid) was carried out via the interfacial technique. Briefly, poly(acrylic acid) was dissolved in water to which an equivalent amount of sodium hydroxide had been added. The aqueous solution of poly(sodium acrylate) was added to a 1-pint Kimax emulsifying jar fitted on top of a Waring Blender. (A detailed description of the polymerization apparatus is given elsewhere.<sup>11</sup>) The cap is screwed on and the blender is turned on. The organic phase containing the organometallic reactant was added through a hole in the jar lid. Stirring time began after all the organic phase had been added. Rapid precipitation of the product occurred. After an appropriate time, the stirring was stopped. The resulting mixture was filtered, washed, and dried under vacuum at about 10°C to  $10^{-2}$  torr.

The amount of organometallic reactant incorporated into the product was determined from knowledge of the amount of unreacted poly(acrylic acid). The aqueous phase washings were acidified with hydrochloric acid, changing poly(sodium acrylate) to poly(acrylic acid). The aqueous solution was evaporated under vacuum. The resulting solid was rapidly washed with water to dissolve the salts present. (Under these conditions it takes 3 or more hours for poly(acrylic acid) to dissolve.) The remaining solid, which was taken to be unreacted poly(acrylic acid), was dried and weighed. Infrared spectra were obtained to assure that the material remaining was unreacted poly(acrylic acid). From knowledge of the amount of unreacted poly(acrylic acid) and the weight of product it is possible to determine the amount of organometallic reactant incorporated into the

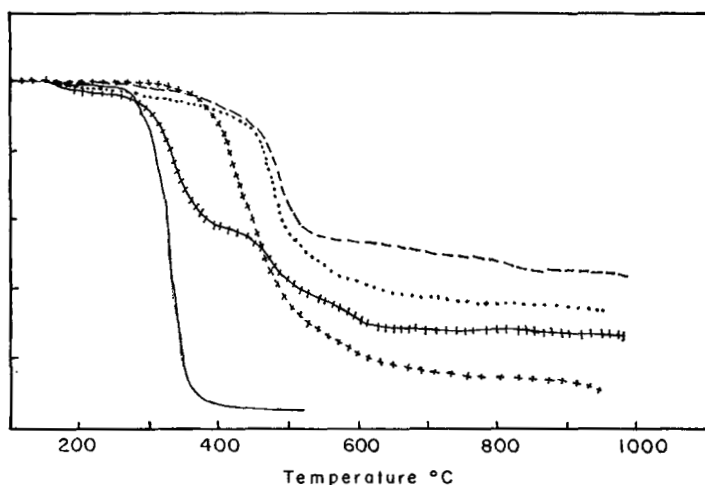


Fig. 1. TGA thermograms for products from the condensation of poly(sodium acrylate) with various Group IVA reactants with a heating rate of 30°C/min in air, where the Group IVA reactants are: (-----) triphenyltin chloride; (—) triphenylsilicon chloride; (▨▨▨▨) diphenyltin dichloride; (+++++) diphenylsilicon dichloride; (.....) dibutyltin dichloride. Gas flow rates in both air and nitrogen for both the TGA and DSG measurements were about 0.3 l./min.

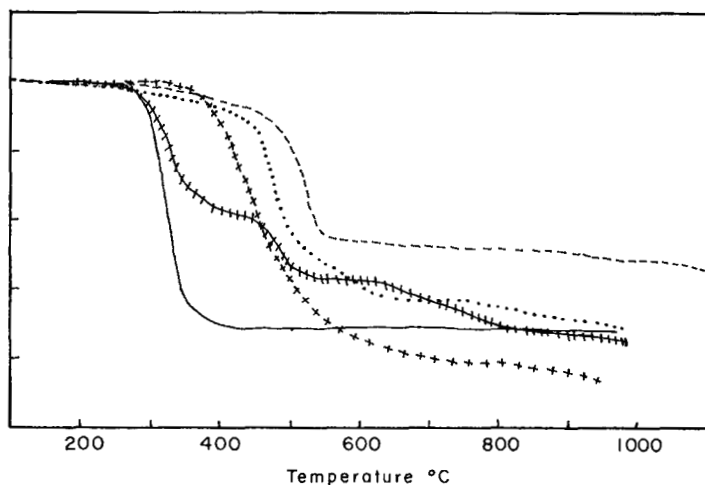


Fig. 2. Same as Fig. 1, except that measurements were obtained in nitrogen.

polymer. In some instances, it was possible to recover the unreacted organometallic reactant from the organic phase and to determine from this the amount which had reacted with the poly(sodium acrylate). The amounts of organometallic reactant incorporated into the polymer as determined by both methods agreed closely with one another. Polymer solubility was studied by adding about  $10^{-3}$  g of product to 3 ml of liquid.

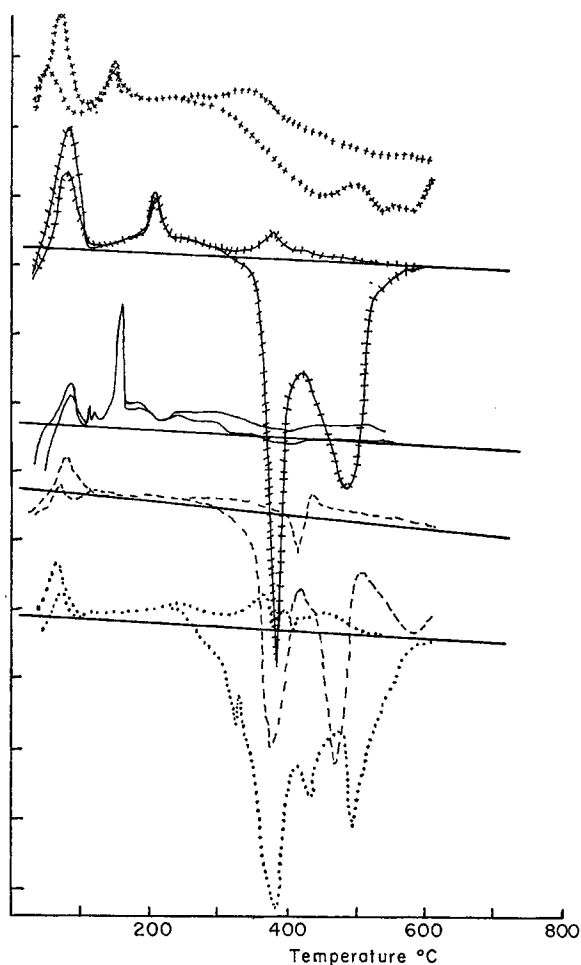


Fig. 3. DSC thermograms taken for the products mentioned in Fig. 1. Measurements obtained in nitrogen and air at a heating rate of  $30^{\circ}\text{C}/\text{min}$  on samples weighing about 0.00100 g with an Y-axis sensitivity of  $0.2^{\circ}\text{C}/\text{in.}$  (each division marked on the Y-axis represents 1 in.). The  $\Delta T = 0$  line is designated, where known, as a straight line. Lines below the  $\Delta T = 0$  line represent exothermic transitions whereas lines above represent endothermic transitions. Markings are the same as those given in Fig. 1.

The liquid-polymer mixtures were observed over a period of two weeks.

The resulting modified poly(acrylic acid) was studied using the Beckman IR-10 and the Perkin-Elmer IR 237-B, using KBr pellets for the solids. The spectra were in agreement with that which would be expected.

Thermal gravimetric analysis (TGA) was carried out using a du Pont 950 TGA (Figs. 1 and 2). Differential scanning calorimetry (DSC) was conducted employing a du Pont 900 thermal unit with a du Pont DSC cell (Fig. 3). A linear baseline compensator was used with the DSC cell to insure a constant energy baseline. A Mettler H20T semimicro balance was

used for the DSC sample weighings. DSC measurements were obtained on samples contained in an open aluminum cup to allow the free flow (away from the solid) of volatilized gases, thus more closely simulating the conditions under which TGA studies were conducted. A gas flow rate (air and nitrogen) of about 0.3 l./min was maintained for both the DSC and the TGA studies. The samples were ground to aid in obtaining reproducible results.

## DISCUSSION AND RESULTS

Recently, we have been studying the synthesis of Group IVA polyesters of form I.<sup>1-3,13,14</sup> The work presented here is an extension of this study.

Inclusion of the organometallic moiety into the polymer side chain is not general. Tables I and II illustrate systems where inclusion has been effected. We were unable to effect such inclusion with other Group IVA reactants. The list of reactants not successfully included into poly(acrylic acid) includes the following: tri-*n*-butyltin chloride; tri-*n*-propyltin chloride; trimethylsilicon chloride; dimethylsilicon dichloride; phenylmethylsilicon dichloride; methylhydrogensilicon dichloride; and methylvinylsilicon dichloride.

The reaction site in PAA systems is believed to be very near the interface of the two solvents or in the aqueous layer because of the insolubility of the acid salt in the organic phase. As a side observation, we have been unable to effect the inclusion of mono- and dichlorophosphates and phosphonates into the poly(sodium acrylate).<sup>19</sup> We were also unable to effect the synthesis of linear polyesters via reaction of dichlorophosphates with diacid salts.<sup>19</sup> The reactants recovered from both the aqueous and organic phases are the hydrolyzed phosphorus and unreacted poly(sodium acrylate). This agrees with the thought that condensation with poly(sodium acrylate)

TABLE I  
Products from Poly(sodium Acrylate)<sup>a</sup>

Organometallic reactant	Yield, %	Organometallic reactant included in product, mole-%	Softening Range, <sup>b</sup> °C
Dibutyltin dichloride	76	49	
Triphenyltin chloride	48	33	
Diphenyltin dichloride	47	31	
Diphenylsilicon dichloride	88	49	138-140
Triphenylsilicon chloride	42	20	148-152

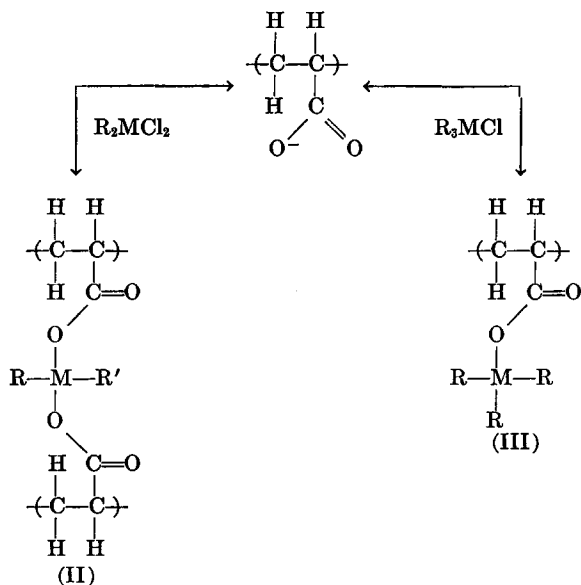
<sup>a</sup> Reaction conditions: 0.003 moles poly(sodium acrylate) in 50 ml water condensed with the organometallic reactant in 50 ml CHCl<sub>3</sub> with stirring at 17,500 rpm (no load) at 25°C, with 30 sec stirring time.

<sup>b</sup> Except in those instances where softening ranges are recorded, the material remained solid to 300°C.

occurs near the interface or in the aqueous phase where rapid hydrolysis of the phosphorus reactant occurred in preference to condensation with the polymer. Most interfacial condensations are reported to occur in the organic phase, but these have included only organic soluble reactants in the aqueous phase.<sup>12</sup> Unreacted poly(sodium acrylate) can be quantitatively recovered from these reaction systems, indicating that inclusion of the phosphorus moiety does not occur.

There are not enough positive results to allow a confident comparison of reactivity as the metal is varied.

The structure of the products from the condensation reaction with poly(sodium acrylate) was as expected. The difunctional reactants yield crosslinked products while the monofunctional reactants yield linear polymers (as illustrated in structure II and III, respectively). The linear polymers are generally soluble in dipolar, aprotic solvents such as dimethyl sulfoxide, dimethylformamide, and acetone (slightly). Both the crosslinked and linear polymers degrade in strong acids such as concentrated sulfuric acid. Products from dihalo reactants are insoluble in all tested solvents, which is in agreement with the proposed crosslinked nature:



The reaction was rapid, with the yield and the organometallic reactant inclusion being constant after 30 sec or less (Table II). The amount of Group IVA component incorporated into the polymer was calculated as described in the experimental section. The inclusion of the organometallic moiety can be considered to be in the average to high range. A 50 mole-% inclusion would result if each carboxylate unit reacted with one Group IVA monochloride unit; and for a crosslinked product (i.e., systems employing a difunctional halide organometallic reactant), a 50 mole-% inclusion would result if every two carboxylate units contained one organometallic moiety.

The materials are glassy and can be ground to give a powdery material. Some products form tough, flexible films when originally recovered and dried or when cast from solvents such as acetone.

Some generalized observations can be made concerning the thermal properties of the modified poly(acrylic acid) products. As found for other similar organometallic products, stability (with respect to weight retention) is generally of the order  $N_2 > \text{air}$  and crosslinked  $> \text{linear}$ .

Mechanisms for degradation vary between whether the metal is tin or silicon. For instance, the product utilizing triphenylsilane chloride undergoes degradation via an endothermic pathway which is identical in air and  $N_2$  to about 250°C. At 275°C, there is a 30% weight residue in  $N_2$  but only

TABLE II  
Results as a Function of Reaction Time for Poly(acrylic Acid)\*

Group IVA reactant	Reaction time, sec	Yield, %	Group IVA inclusion, mole-%
Dibutyltin dichloride	30	72	47
	60	76	49
	120	76	49
	180	77	49
Triphenyltin chloride	30	46	31
	60	48	33
	180	48	33
Diphenylsilicon dichloride	30	87	49
	60	88	49
	180	88	49
Triphenylsilicon chloride	30	41	20
	60	42	20
	180	42	20

\* Reaction conditions: 0.003 moles poly(sodium acrylate) in 50 ml water condensed with the organometallic reactant in 50 ml  $CHCl_3$  with stirring at 17,500 rpm (no load) at 25°C, with a variation in stirring time.

a 8% weight residue in air. No further changes in the DSC (to 600°C) and TGA (to 850°C) occur in air or  $N_2$ . The analogous product from triphenylstannane chloride undergoes degradation via distinctively different pathways in air and  $N_2$ . Degradation in air occurs via a highly exothermic pathway, probably occurring with oxidation.<sup>15</sup> This may mean that tin is either oxidized or catalyzes oxidation, whereas silicon does not. Caution must be exercised in any application of such observations since so few products have been studied.

The products remain solid to at least 600°C as detected via visual observation. The degradation products (solid residues) are generally white and powdery in nature.

Portions of this paper were taken from the Ph.D. Thesis of John D. Piersma.

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