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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Production of Organometallic Polymers by the Interfacial Technique. XXXII. Reaction Variables in the Synthesis of Oligomeric Tin Poly(cobalticinium Esters) and Thermal Properties of the Products

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To cite this Article Carraher Jr., Charles E. , Peterson, George F. , Sheats, John E. and Kirsch, Ted(1974) 'Production of Organometallic Polymers by the Interfacial Technique. XXXII. Reaction Variables in the Synthesis of Oligomeric Tin Poly(cobalticinium Esters) and Thermal Properties of the Products', *Journal of Macromolecular Science, Part A*, 8: 6, 1009 – 1022

To link to this Article: DOI: 10.1080/00222337408066416

URL: <http://dx.doi.org/10.1080/00222337408066416>

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Production of Organometallic Polymers by the Interfacial Technique. XXXII. Reaction Variables in the Synthesis of Oligomeric Tin Poly(cobalticinium Esters) and Thermal Properties of the Products*

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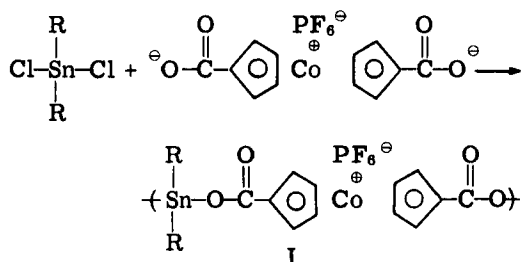
ABSTRACT

The synthesis of oligomeric tin poly(cobalticinium esters) is presented as a function of the particular reaction variables stirring rate, pH and amount of added base, mole ratio of

*Presented at the 166th American Chemical Society Meeting in Chicago.

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reactants, concentration of reactants, and volume of organic phase. Factors which decrease the solubility of the stannane apparently act to increase the yield of polyester.

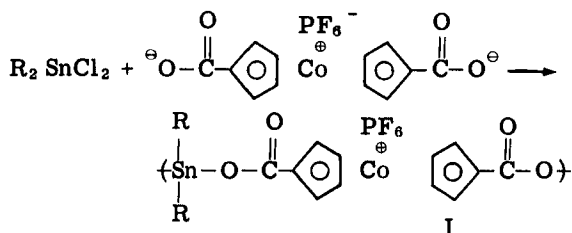


The thermal characterization of I was carried out via DSC and TGA. The products generally exhibit endotherms below 150 to 200°C which may be related to T_g . Above 200°C, degradation occurs in air by an oxidative mode.

INTRODUCTION

The synthesis of difunctional cobalticinium salts suitable for use in condensation polymerizations was recently accomplished [1, 2]. Inclusion of the cobalticinium moiety into polymers is just beginning [3-7].

Recently we reported the synthesis of oligomeric tin poly(cobalticinium esters) utilizing the interfacial technique [6]. We now report the dependency of synthesis on particular reaction variables and on the thermal behavior of the products.



Possible reasons for desiring the inclusion of tin and the cobalticinium moiety into polymers are given elsewhere [6, 8, 9].

EXPERIMENTAL

Reaction and isolation procedures are similar to those given in detail elsewhere [10, 11]. Briefly, aqueous solutions of 1,1'-bis-(carboxyl)cobalticinium hexafluorophosphate with added base were added to rapidly stirred organic solutions containing $R_2 SnCl_2$. Polycondensations were conducted in a 1-pt Kimax emulsifying jar placed on a Waring Blender. The reactants were added through a large-mouthed funnel placed through a hole in the jar cap. The 1,1'-bis-(carboxyl)cobalticinium hexafluorophosphate (BCHFP) was prepared as described elsewhere [1, 2, 5]. The dihalo tin compounds were used as purchased from Alfa Inorganics, Beverly, Massachusetts. The desired amount of base is accomplished by addition of a specified amount of 0.1M NaOH to the diacid, followed by dilution with distilled water to the desired volume.

Basic elemental and spectral analyses were given previously [6].

Polymerizations in which the stirring speed was varied utilized a blender where the stirring speed was standardized using a Stobotac Type 1531-A (General Radio Co., Concord, Connecticut). The blender was connected to a Powerstat Type 116 (Superior Electric Co., Bristol, Connecticut) and the "no-load" speed was measured as a function of powerstat reading.

The pH of the aqueous solutions was measured using a Corning (Model 5) pH meter.

Thermal gravimetric analysis (TGA) was conducted employing a 950 DuPont TGA. Differential scanning calorimetry (DSC) was carried out employing a Du Pont 900 DSC cell fitted to a Du Pont 900 Thermal Analyzer console using a linear baseline compensator to insure a constant energy baseline. A Mettler H20T semimicrobalance was employed for the weighings of the DSC samples. Measurements were obtained on samples contained in open aluminum cups to allow the free flow away from the solid of volatilized materials, thus closely simulating the conditions under which the TGA studies were conducted. Air and nitrogen flows of about 0.3 liter/min were employed.

DISCUSSION AND RESULTS

Reaction Variables - Condensation of BCHFP with Diplenyln Dichloride

Product yield at constant stirring time and product molecular weight are often used as indices in determining the dependency of the condensation process on reaction variables. Tin poly(cobalticinium

esters) are essentially insoluble in all organic liquids. Several tin poly(cobalticinium esters) exhibited limited solubility in the range of 0.1 to 0.01% in dipolar aprotic solvents such as acetone, dimethylformamide, and dimethylsulfoxide. This is below the generally recognized range for reliable molecular weight determinations. Sample η_{sp}/c readings were to 0.10 dl/g with number-average degrees of polymerization by the Rast method to 50 and degrade rapidly (time < 3 min) in aqueous salt solutions. The lack of adequate solubility is unfortunately characteristic of many of the thus far synthesized organometallic polymers and oligomers [12] and prevents using molecular weight to characterize the polymers. (Noncobalticinium tin polyesters are generally soluble in polar solvents and are oligomeric, exhibiting number-average degrees of polymerization in the range of 5 to 50. The present products are also probably oligomeric [10-12].) Thus only product yield will be used to determine the effects that particular reaction variables have on the polymerization process.

Yield was studied as a function of pH and amount of base to evaluate the importance of these parameters. Anion exchange with the BCHFP before reaction is important. When buffers were employed to maintain pH, IR spectra of the products exhibited bands characteristic of the anion groups of the buffer. This discouraged the use of buffered systems since the products were mixtures containing several associated anions.

Anion exchange is also significant when employing NaOH if the BCHFP is permitted to reside in the basic solution for 10 min or longer. If BCHFP-NaOH solutions are prepared just prior to reaction, no anion exchange is detected. Yield as a function of pH is given in Table 1. Although the BCHFP is a reasonably strong acid ($K_1 = 1.2 \times 10^{-2}$ $K_2 = 1.5 \times 10^{-3}$), base is needed to convert it to the dianion, presumably the most reactive species. Neutralization of the acid is not the only important role filled by the added base, since yield remains fairly constant even after enough base to neutralize all of the diacid is added. Yield "jumps" around a 1.7:1 base:-COOH ratio, giving a maximum around a 2.9:1 ratio of base:-COOH.

IR spectra of samples from runs where pH is increased show a progressive increase in size of the carbonyl peak at 1620 cm^{-1}

$$\begin{array}{c} \text{O} \\ || \\ \text{Sn-OC-} \end{array}$$
 group) and the twin peaks at 735 and 690 cm^{-1} (C_6H_5 groups), and a progressive decrease in size of the carbonyl group at 1730 cm^{-1} (CO_2H groups). This trend indicates that fewer BCHFP end groups are present and that more of the diphenyltin moiety has been included in the polymers as pH is increased. Since the size and shape of the SnOH peak at 3300 to 3500 cm^{-1} remains the same, these trends are

TABLE 1. Yield as a Function of Added Base and pH^a

Moles of sodium hydroxide added	pH ^b	Yield (%)	Equivalence of base
0.00	-	0	0
0.45	3.1	8	0.75
0.50	3.2	7	0.83
0.55	5.8	10	0.91
0.56	6.8	9	0.93
0.58	9.6	8	0.95
0.60	10.4	7	1.00
0.65	10.9	8	1.08
0.75	11.3	10	1.25
1.00	11.7	30	1.66
1.25	11.8	39	2.08
1.50	12.0	40	2.50
1.75	12.1	46	2.92
2.50	12.2	26	4.17

^aDiphenyltin dichloride (0.300 mmole) in 25.0 ml of chloroform added to stirred solutions of BCHFP (0.300 mmole) in 25.0 ml aqueous solution to which NaOH had been added; 60 sec stirring time; 25°C; 23,500 rpm stirring rate.

^bpH of aqueous phase after BCHFP and base are added, measured using a Corning Model 5 pH meter.

probably not caused by an increase in SnOH end groups but rather by increased chain length. Spectra demonstrating this trend appear in Fig. 1.

Subsequent studies involved the use of more than an equivalence of base since it was determined that a higher product yield is achieved under such conditions (Table 1).

Condensation of BCHFP with dihalostannanes is dependent on the nature of the organic solvent. If carbon tetrachloride is used, products are obtained from a variety of stannanes, but when chloroform was

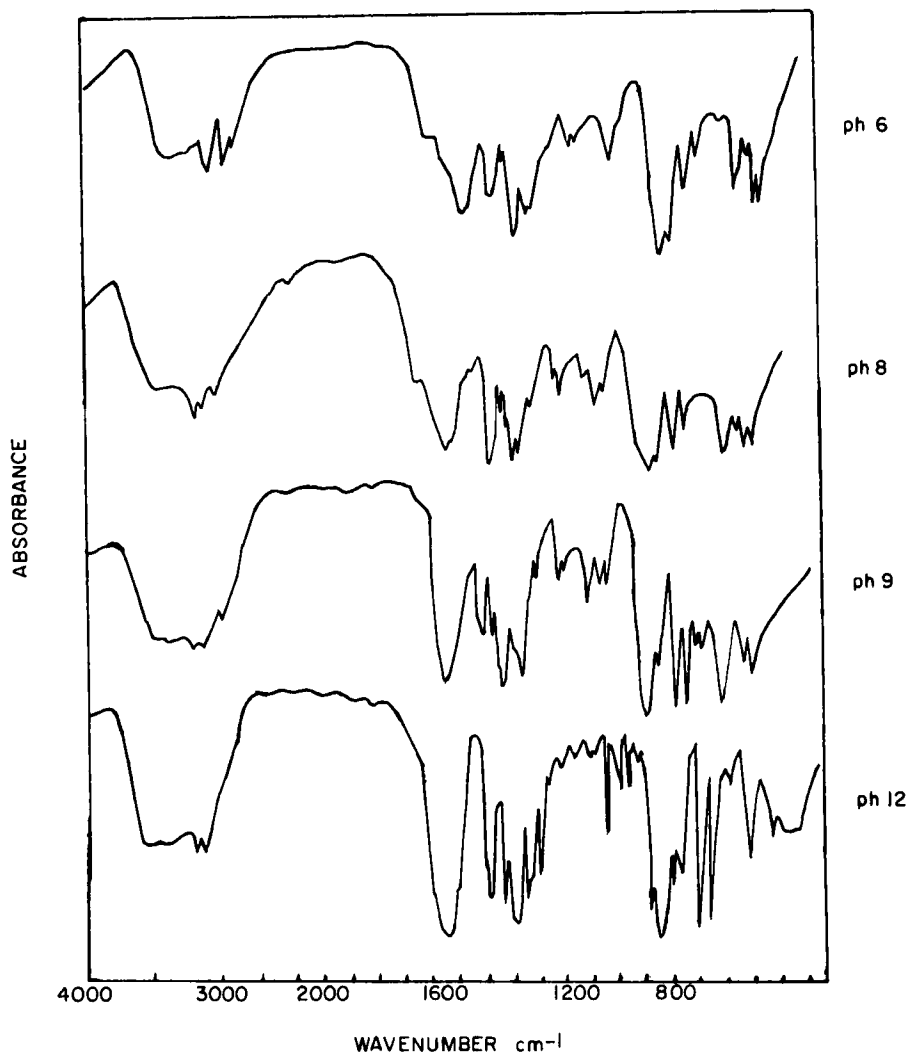


FIG. 1. Variation in the IR spectra of polymers made at various pH's where BCHFP and diphenyltin dichloride were the monomers.

TABLE 2. Yield as a Function of the Concentration of Reactants^a

Concentration (moles/liter of one phase; $\times 10^3$)	Yield (%)
1.0	7
3.0	20
6.0	26
12.0	31
15.0	38
24.0	49

^aReaction conditions: BCHFP and 3.3 equivalence of sodium hydroxide in 25 ml of aqueous solution with diphenyltin dichloride in 25 ml of chloroform at 25°C and 21,000 rpm stirring rate for 1 min stirring time. The mole ratio of reactants is held constant for all systems at 1:1.

used, polymers were formed only with diphenyl and di-*t*-butyl-dihalostannanes, the two stannanes which gave the best yields in carbon tetrachloride [6]. Since the dihalostannanes are more soluble in chloroform, they are less readily extracted into the aqueous phase where the reaction can take place.

The afore suggests that stannane solubility may be a critical parameter. Tables 2 to 4 summarize studies where the concentration, and presumably the solubility of the stannane, is varied. In Table 2 the reactant ratios and solvent volumes remained constant but concentration of the two reactants was varied. Yield increased with increased concentration. In Table 3 the concentration and volume of the aqueous phase remained constant but the volume of the chloroform varied. Yield decreased as chloroform volume increased. Other factors are also probably being varied, such as interfacial area and concentration ratio of BCHFP:stannane. Thus while the decreased yield with increase in the volume of chloroform is consistent with the idea that factors which decrease stannane solubility exhibit positive influences in product yield, other factors may be responsible for the observed trend.

TABLE 3. Yield as a Function of the Volume of Chloroform^a

Volume of CHCl ₃	Yield (%)
5.0	40 ^b
10.0	63
15.0	57
20.0	56
25.0	55
50.0	16

^aReaction conditions: 0.300 mmole of BCHFP and 0.875 mmole of NaOH were added to 15.0 ml of water; 0.300 mmole of diphenyltin dichloride were added to the given amounts of CHCl₃; stirring time 60 sec. Stirring rate, 23,500 rpm at 25°C.

^bThe volume of the two phases was too small for proper stirring.

TABLE 4. Yield as a Function of the Mole Ratio of Reactants: BCHFP Varied^a

Molar ratio BCHFP:diphenyltin dichloride	Concentration of BCHFP (mole/liter)	Yield (%)
1:4	0.00417	27
1:2	0.00835	21
1:1	0.0167	50
1.5:1	0.0250	42
2:1	0.0334	70

^aReaction conditions: Diphenyltin dichloride (0.250 mmole) in 15.0 ml of chloroform added to 15.0 aqueous solutions of BCHFP with 2.9 times the molar amount of NaOH added, 60 sec stirring time at 23,500 rpm stirring rate at 25°C.

TABLE 5. Yield as a Function of the Mole Ratio of Reactants: Diphenyltin Dichloride Varied^a

Molar ratio BCHFP:diphenyltin dichloride	Concentration of diphenyltin dichloride (mole/liter)	Yield (%)
4:1	0.00417	42
2:1	0.00834	47
1:1	0.0167	50
1:2.3	0.0396	58
1:2.4	0.0406	39
1:3	0.0501	33

^aReaction conditions: diphenyltin dichloride in 15.0 ml of chloroform added to 15.0 ml aqueous BCHFP (0.250 mmole) to which NaOH (0.875 mmole) had been added; 1 min stirring time at 25°C, and 23,500 rpm stirring rate.

In Table 4 the molar amount of BCHFP was varied while the dihalostannane concentration remained constant, and in Table 5 the dihalostannane concentration was varied while the BCHFP remained constant. (Yields are reproducible to about $\pm 2\%$.) The trend is not clear, but the best yields appear to be obtained with equal molar amounts or a slight excess of BCHFP.

Yield was studied as a function of stirring rate. Yield increased with increased rate of stirring (Table 6). Situations such as these are referred to as "diffusion controlled" reactions [13], i.e., difference in the diffusion rate are responsible for the observed differences in yield. This is based on the assumption that as stirring rate increases, droplet size decreases, hence the interfacial surface area increases, resulting in an increased "rate" of diffusion of the reactants to the polymerization site.

It is believed that the reaction occurs in the aqueous phase or near the interface. This is based on the following: first, the presence of

TABLE 6. Yield as a Function of Stirring Rate^a

Stirring rate (rpm)	Yield (%)
7,800	64
12,800	64
17,700	70
24,500	73

^aReaction conditions: 0.418 mmole of diphenyltin dichloride added to 25.0 ml of CCl₄; 0.418 mmole of BCHFP added to 25.0 ml of 0.0584 M NaOH solution; stirring time, 60 sec; temperature, 25°C.

added base is necessary for the reaction to occur (Table 1); second, after the reaction the polymer appears as a gel containing a large amount of water but no chloroform; third, concentration studies (Tables 2 and 3) and solvent studies [6] indicate that the greater the tendency of the stannanes to remain in the organic phase, the lower the yield; fourth, BCHFP and the deprotonated diacid are insoluble in the organic solvents employed.

Thermal Characterization

The products are yellow in color when recovered. The products follow a similar trend of color changing and melting when observed on the heating table of a Fisher-Johns Melting Point Apparatus. They soften to give a tacky material about 180 to 220°C. Most of the materials lighten in color between 250 and 260°C, and by 260 to 280°C a brown coloration appears which increases to a dark brown around 280 to 300°C. A strong odor, believed to be associated with the tin moiety, is emitted above 250°C. (The authors became dizzy and received headaches if they smelled this odor. Thus caution should be exercised when dealing with the products above 250°C.)

Differential scanning calorimetry (DSC) and thermogravimetric (TGA) thermograms of the products appear in Figs. 2 to 4. The DSC thermograms are similar, with the exception of those products containing the dibenzyltin moiety, to 150 to 200°C. All heat changes are

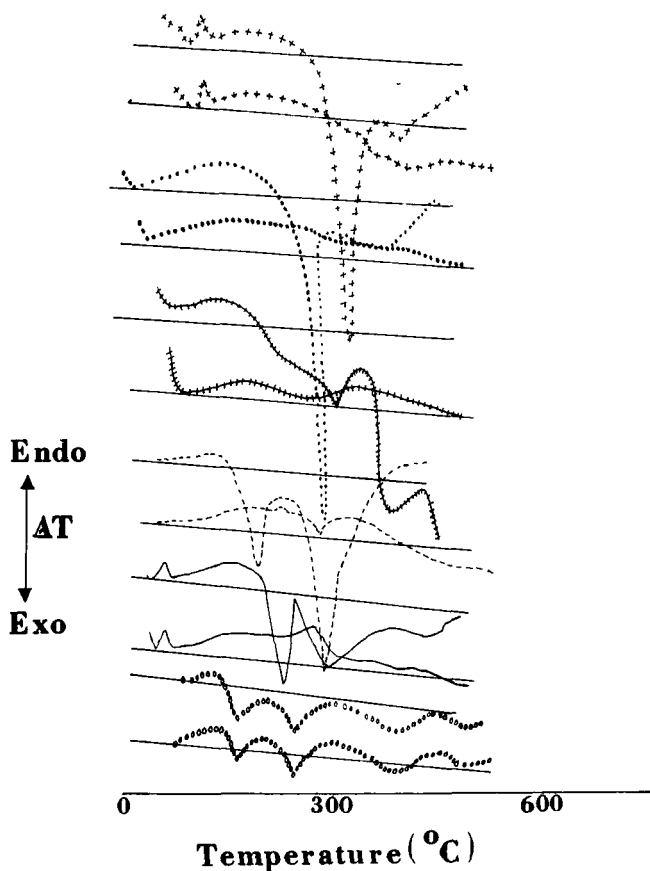


FIG. 2. DSC thermograms of tin poly(cobalticinium esters) in air (upper member of each pair) and N_2 (lower member of each pair) at a heating rate of $30^\circ\text{C}/\text{min}$ with a gas flow rate of 0.3 liter/min on samples weighing 0.00100 ± 0.00002 g with a "Y-axis" reading of $0.5^\circ\text{C}/\text{in.}$ (0.02 mV/in.). The esters are condensation products of BCHFP with dibutyltin dichloride (+ +), diethyltin dichloride (.), divinyltin dichloride (++) , diphenyltin dichloride (- -), dioctyltin dichloride (—), and dibenzyltin dichloride (o o). The solid straight line is the $\Delta T = 0$ line.

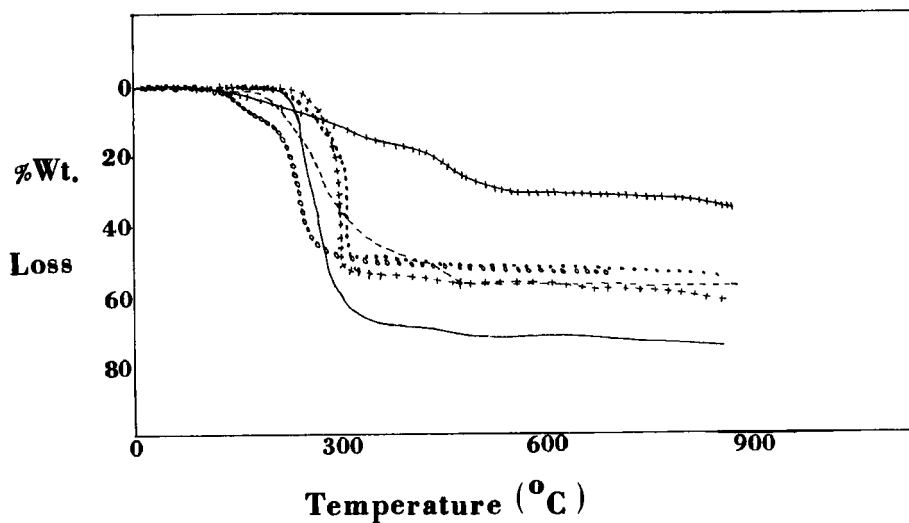


FIG. 3. TGA thermograms in air under conditions described in Fig. 2 for heating rate, gas flow rate, sample weight, and product designations.

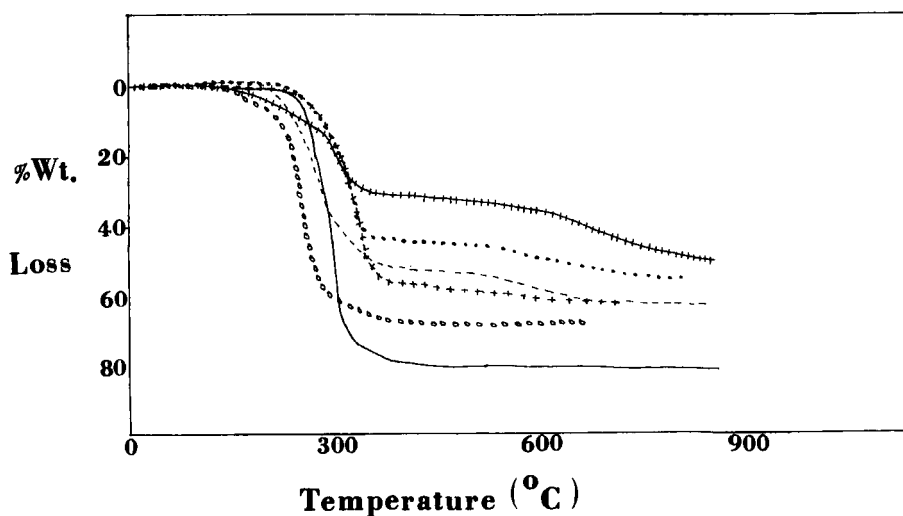


FIG. 4. TGA thermograms in nitrogen under conditions described in Figs. 2 and 3.

endothermic in this region and with no marked difference with respect to the atmosphere. IR spectra of products heated to 150°C are identical to those of the unheated products. Also no weight changes are observed in the TGA thermograms in this region. Thus the heat absorbed in this region is involved in a physical change as opposed to a chemical change, and may be connected to a glass transition range for the products.

Above 200°C the thermograms are dissimilar with a correspondence between TGA and DSC thermograms. The energy changes observed via DSC correspond to weight losses observed in the TGA thermograms. The energy changes, via DSC, are largely exothermic; whereas those in nitrogen are largely endothermic. This behavior is characteristic of degradation occurring in air by oxidative modes.

The initial weight loss is large, often about 50%. This is followed by a gradual weight loss to the final temperature. The shapes of the TGA thermograms are dependent on the heating rate, i.e., they are kinetically controlled.

ACKNOWLEDGMENT

J.E.S. and T.K. were supported by a Research Corporation Federich Gardner Cottrell Grant.

REFERENCES

- [1] J. Sheats and M. Rausch, J. Org. Chem., **35**, 3245 (1970).
- [2] J. Sheats and T. Kirsch, Syn. Inorg. Metal-Org. Chem., **3**, 59 (1973).
- [3] C. Pittman, O. Ayers, S. McManus, J. Sheats, and C. Whitten, Macromolecules, **4**, 360 (1971).
- [4] C. Carraher and J. Sheats, Org. Coatings and Plastics Chem., **33**, 634 (1973).
- [5] C. Carraher and J. Sheats, Makromolekulare Chemie, **166**, 23 (1973).
- [6] C. Carraher, G. Peterson and J. Sheats, Org. Coatings Plast. Chem., **33**, 427 (1973).
- [7] T. Ito and T. Kenjo, Bull. Soc. Chem. Japan, **41**, 614, 1600 (1968).
- [8] E. Fischer and G. Herberich, Chem. Ber., **94**, 1517 (1961).
- [9] T. Gill and L. Mann, J. Immunology, **96**, 906 (1966).
- [10] C. Carraher and R. Dammeier, J. Polym. Sci., **A-1**, **8**, 3367 (1970).
- [11] C. Carraher and R. Dammeier, Makromol. Chem., **135**, 107 (1970).

- [12] C. Carraher, Inorg. Macromol. Revs., 1, 271 (1972).
- [13] O. Smirnova, E. Alikhason, J. Loser, and G. Koleshihov, Vysokomol. Soedin., 7, 503 (1965).

Accepted by editor January 28, 1974

Received for publication March 1, 1974