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# PREPARATION OF AROMATIC POLYESTERS OF HINDERED PHENOLS BY ACID INTERCHANGE POLYCONDENSATION.

## 2. METAL SALT CATALYSIS

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### ABSTRACT

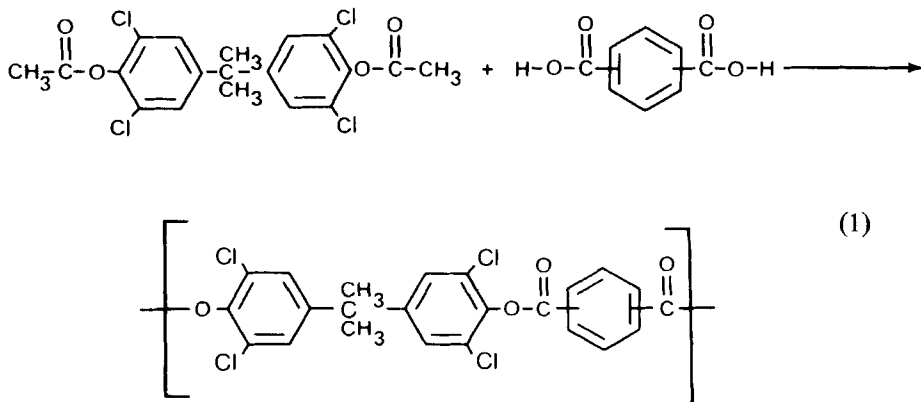
The effect of the addition of metal salts as catalysts for the acid interchange polycondensation of tetrachlorobisphenol A diacetate with phthalic acids was examined. The acetate salts of some transition metals were found to have an effect upon the molecular weights of the polyesters produced, but inherent viscosities above 0.50 dL/g were not achieved with these catalysts. Modification of the nature of the salts by either the use of a mixture of acetate and strong acid anionic species, or by addition of an equivalent of strong acid to the metal acetate, to generate a mixed salt *in situ*, gave the most effective catalyst for the polycondensation. Inherent viscosities as high as 0.82 dL/g were achieved with a catalyst system consisting of an equimolar mixture of nickel acetate and nickel perchlorate. As an approach to explaining the activity of the metal salt catalysis, it is proposed that a metal salt complex, consisting of a central divalent, tetracoordinate transition metal, surrounded by the oxygens from the phenyl acetates and from the incoming carboxylic acid, orients the reactants and facilitates transfer of acid functions.

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## INTRODUCTION

The previous paper in this series [1] described the effects of various solvents upon the transacylation polycondensation of mixed iso- and terephthalic acids with tetrachlorobisphenol A diacetate.



The reaction when conducted as a melt polycondensation is limited to very low molecular weights, at least partially due to the high melting point and high melt viscosity of the polymer. In addition, the reaction frequently yields only highly colored products [2]. Temperatures required to carry out the condensation to high molecular weights are generally in the range of the thermal decomposition points of the polymers and thus lead to only degraded products. Benzophenone or diphenyl ether were found to be useful as reaction media for this system, leading to solutions or plasticized melts at temperatures of about 260°C, which are capable of being driven to polymers of appreciable molecular weight.

Most polycondensation processes are carried out in the presence of catalysts. In the conventional ester interchange condensation, which is widely used for the preparation of glycol phthalate polyesters (PET, PBT, etc.), a number of acid and metal salt catalysts have been found to be active. Among the salts described are alkaline and alkaline earth oxides and hydroxides, antimony oxide, zinc acetate, and transition metal acetates [3]. In addition, the transacylation reaction for the preparation of all aromatic polyesters has been reported to be catalyzed by similar compounds, as well as by active metals such as magnesium, which are probably rapidly converted to the acetates in the reaction mixture. Acidic compounds show little catalytic activity but basic compounds accelerate the condensation [4]. Among the com-

pounds described in the literature are alkali and alkaline earth metals, their oxides and hydroxides, amines, zinc oxide, lead oxide, etc. [5]. While these compounds have been found to be effective in the promotion of condensation of nonhindered diphenols with free acids, Temin concluded that they were ineffective for the preparation of high molecular weight polyesters from sterically hindered diphenols [6].

## EXPERIMENTAL

### Materials

Tetrachlorobisphenol A (TCBPA) was purchased from Dover Chemical Co., Dover, Ohio. Terephthalic acid was purchased from Aldrich Chemical Co. and from Amoco Chemical. Isophthalic acid was received from either Aldrich or from Arco Chemical. Metal salts were purchased from the Alpha Division of Ventron. Solvents were purchased from Fisher Scientific. Tetrachlorobisphenol A diacetate (TBA) was prepared as reported earlier [1].

### Polycondensation

The polycondensation reactions were carried out as previously reported [1].

The optimized polymerization procedure which resulted from this work is as follows.

### Preparation of Catalyst Solution

To a 250-mL Erlenmeyer flask is added 100 mL acetic anhydride, 1.14 g (0.005 mol) nickel acetate tetrahydrate, and 1.45 g (0.005 mol) nickel nitrate hexahydrate. The mixture is stirred at 50°C for 3 h to dissolve the salts completely. The clear green solution is used as the polymerization catalyst in the following polymerization procedure and is assumed to contain 0.01 mol Ni/mL.

### Polycondensation

To a 250-mL three-necked flask equipped with a stirrer, nitrogen inlet, and distillation head is added 46.0148 g (0.1 mol) TBA, 11.6294 g (0.07 mol) isophthalic acid, 4.9840 g (0.03 mol) terephthalic acid, 100 mL diphenyl ether,

and 0.5 mL of the nickel acetate/nickel nitrate catalyst solution. The stirrer shaft is connected to a constant-speed motor equipped with a torque meter (Master Servodyne, Cole Parmer Co.) in order to monitor the viscosity increase. The reaction flask is heated by means of a silicone oil bath to 200°C. At this temperature, acetic acid begins to distill from the reaction mixture, and the acids begin to dissolve. The temperature is increased to 250-260°C, and after about 1 h total reaction time all of the acids have dissolved as evidenced by the reaction mixture clearing. The temperature of the oil bath is increased to 300°C, and the diphenyl ether is allowed to reflux in the lower portion of the distilling head while acetic acid continues to distill slowly. After about 2-4 h, the rate of the nitrogen sweep through the flask is increased, and diphenyl ether is distilled from the viscous reaction mixture. When stirring is no longer possible due to the high viscosity, a vacuum is applied to remove the remaining diphenyl ether. The vacuum is released with nitrogen, the oil bath removed, and the polymer allowed to cool under nitrogen.

### Characterization

Inherent viscosities were determined either by a conventional dilute-solution method using a 0.1% solution in 10/7 (w/w) phenol/tetrachloroethane solvent or as a 0.1% solution in methylene chloride. Acid contents of the polymers were determined by potentiometric titration, and acetate end groups were determined by NMR spectroscopy.

## DISCUSSION

The initial experiments in this program, which were aimed at demonstration of the feasibility of utilizing the transacylation reaction to prepare polyesters from hindered diphenols, utilized manganese(II) acetate as the transacylation catalyst. While this system served to demonstrate feasibility, the molecular weights of the polymers obtained were not sufficient to give polymer which could be processed to structures with mechanical properties of commercial interest. In an effort to optimize the process, a variety of metal salts were screened for their potential as catalysts for the transacylation polycondensation. Since the earlier work [1] showed that manganese(II) acetate was a relatively effective catalyst for this reaction, the most logical approach seemed to be to investigate the activity of other metal acetates in this system. Prior to a detailed investigation of the effects of variation of the nature of the catalyst components, a number of other experimental modifications

were carried out in attempts to determine which factors might be affecting the molecular weight of the polyester. Among the variables evaluated were purity of the diacetate monomer, method of preparation and purification of the diacetate, reaction stoichiometry, and time of reaction.

### **TCBPA Purity**

In order to investigate thoroughly the effect of trace levels of impurities in TBA upon the polycondensation, a variety of esterification conditions and purification procedures were evaluated. Various acetic anhydride/TCBPA ratios and catalysts were employed; washing of the crude diacetate with water, methanol, and benzene was examined; and recrystallization was carried out. None of the procedures and combinations of procedures seemed to have a significant effect upon either the properties of the TBA or upon the inherent viscosity of the polymer produced. In addition, several grades of TCBPA were used in each of the acetylation procedures. Variation of the sources of TCBPA or purification of this starting material failed to show any effect upon the polymer produced.

### **Phthalic Acid Purity**

Several grades of iso- and terephthalic acids were evaluated. The use of various grades primarily affected only the color of the polymer produced, with little effect on the molecular weight. Some effect on particle size could be seen. It is believed that the rate of solution of terephthalic acid is one of the controlling factors in the rate of Reaction (1). However, the effect on the rate was not quantitatively determined. The least colored polyesters produced in this study were prepared from a high-purity, low-metal-content terephthalic acid from Amoco and a similar high-purity isophthalic acid from Arco.

### **Effect of Stoichiometry**

Acid/diacetate ratios of 0.985, 0.9925, 1.000, 1.0075, and 1.015 were investigated with a manganese acetate catalyst. Deviation of 1.5% in either direction invariably led to lower molecular weight polyester. The 1:1 stoichiometry gave the highest molecular weight, with a slight positive effect being seen in a few polycondensations for an acid-deficient system (0.9952). Since none of the monomers in question is particularly volatile, these results are not sur-

TABLE 1. Catalytic Effect of Metal Salts on Transacylation Product

Metal salt	$\eta_{inh}$ , dL/g <sup>a</sup>
Mn(OAc) <sub>2</sub>	0.51
Co(OAc) <sub>2</sub>	0.53
Ni(OAc) <sub>2</sub>	0.47
Cu(OAc) <sub>2</sub>	0.37
Hg(OAc) <sub>2</sub>	0.24
Si(OAc) <sub>4</sub>	0.38
Zn(OAc) <sub>2</sub>	0.39
Pb(OAc) <sub>2</sub>	0.24
Ag(OAc)	0.40
Cd(OAc) <sub>2</sub>	0.30
Rb(OAc) <sub>2</sub>	0.28
In(OAc) <sub>2</sub>	0.32
Cs(OAc) <sub>2</sub>	0.25
Na(OAc)	0.18
None	0.25

<sup>a</sup>Determined at 0.1% in 10/7 phenol/tetrachloroethane.

prising, but they could be a drawback to the commercial application of the process. The lack of flexibility to slight deviations from exact stoichiometry may lead to an unacceptably degree of variability in the product.

Table 1 lists the various metal acetates evaluated. It can be seen that many of the salts evaluated failed to influence the molecular weight of the recovered polyester. Without any metal salts present, inherent viscosities of 0.2 dL/g could be achieved for the TBA phthalic acids system in diphenyl ether. The polymers of highest inherent viscosity were obtained with the acetate salts of manganese(II), cobalt(II), and nickel(II). The effect of salts of other transi-

TABLE 2. Effect of Catalyst Level on Inherent Viscosity of Polymer

Metal acetate	Catalyst level, mol% <sup>a</sup>	$\eta_{inh}$ , dL/g <sup>b</sup>
Co(OAc) <sub>2</sub>	1	0.19
	0.4	0.21
	0.2	0.30
	0.04	0.24
	0.02	0.37
	0.02	0.41
	0.02	0.53
	0.004	0.53
Mn(OAc) <sub>2</sub>	0.8	0.24
	0.4	0.32
	0.2	0.28
	0.08	0.34
	0.02	0.44
	0.02	0.49
	0.02	0.51
Ni(OAc) <sub>2</sub>	0.2	0.25
	0.04	0.35
	0.04	0.40
	0.02	0.47

<sup>a</sup>Based on total acid charged.

<sup>b</sup>Determined on 0.1% solution in 10/7 phenol/tetrachloroethane.

tion metals can be seen in that copper, silver, and zinc also appear to have a positive, though smaller, effect upon the molecular weight.

No dramatic effect of the metal salt level was found (Table 2). While the highest inherent viscosities were obtained at metal salt levels of 0.01-0.04%, higher salt levels caused only a modest drop in molecular weight. One possible explanation for this could lie in the reaction of the metal salt with the



aromatic carboxylic acid, leading to the precipitation of acid and, hence, a stoichiometric imbalance.

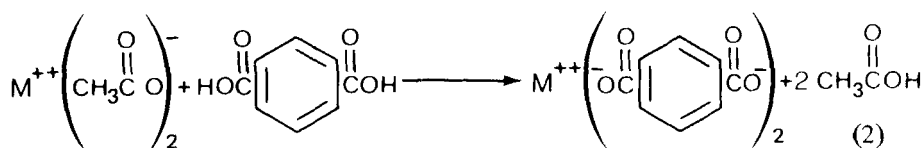
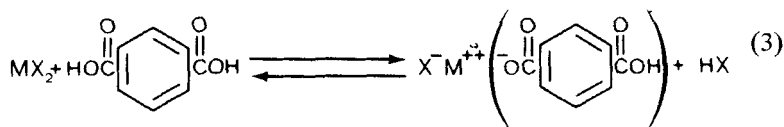


Table 2 also indicates the degree of reproducibility attained. In addition to the normal experimental variation which is common in such laboratory polycondensations, variations were found to arise from the method used for inherent viscosity determination, as well as from the polymerization technique employed. Differences of  $\pm 15\%$  in the inherent viscosity for apparently identical experiments were found. While the degree of error in the inherent viscosity would not be significant for polymers of high MW, at the low MW that we obtained in many of the early experiments, the variation was appreciable, and observation of small differences due to changes in the nature and levels of salt catalysts were difficult and required multiple experiments.

Table 3 shows the effect of the anion of the metal salt. In general, slightly higher inherent viscosities were obtained with the acetate salts than with the salts of stronger mineral acids. As described above, it would be expected that the acetates would be converted to the phthalate salts during polymerization, with evolution of acetic acid. The catalyst species, therefore, would be the metal phthalates in some form.



In the presence of strong acid anions, the equilibrium would not favor the formation of phthalate salts, since the equilibrium of Reaction (3) would lie strongly forced to the left, toward the weaker acid. In these cases, phthalate salt formation is suppressed and the inherent viscosities are similar to those in the absence of any metal salt (Table 3). These results led us to the hypothesis that the active catalyst in these polycondensations may be some form of a metal phthalate complex.

In our attempts to derive some rational basis for the effectiveness of one catalyst salt over another, we examined the effect of various properties of the metal ions on the molecular weights of the polymers produced and on the rates of the polycondensation reaction. Figures 1 and 2 represent the relationship between the ionic radii or covalent radii of the metals and the inherent

TABLE 3. Effect of Anion upon Activity of Metal Salts

Metal salt	Catalyst level, mol%	$\eta_{inh}$ , dL/g <sup>b</sup>
ZnO	0.02	0.31
Zn(OAc) <sub>2</sub>	0.01	0.39
ZnCl <sub>2</sub>	0.02	0.32
MnCl <sub>2</sub>	0.01	0.32
Mn(NO <sub>3</sub> ) <sub>2</sub>	0.01	0.22
Mn(OAc) <sub>2</sub>	0.02	0.51
AgNO <sub>3</sub>	0.01	0.37
AgOAc	0.01	0.40
Hg(NO <sub>3</sub> ) <sub>2</sub>	0.02	0.29
Hg(OAc) <sub>2</sub>	0.02	0.24
Co(NO <sub>3</sub> ) <sub>2</sub>	0.1	0.30
Co(OAc) <sub>2</sub>	0.1	0.28
Ni(OAc) <sub>2</sub>	0.05	0.47
NiCl <sub>2</sub>	0.05	0.34
Ni(NO <sub>3</sub> ) <sub>2</sub>	0.05	0.36

<sup>a</sup>Based on total acid charged.

<sup>b</sup>Determined on 0.1% solution in 10/7 phenol/tetra-chloroethane.

viscosity of the polymers produced in their presence. If one assumes that the active catalytic species is an ionically bonded metal phthalate which covalently complexes the ester functionality of the TBA, then both the ionic and covalent radii (or an intermediate radius based on both) might be expected to affect the polymerization results. The data appear to indicate that the highest molecular weights are obtained with metals with covalent radii of less than 1.2 Å and ionic radii in the range of 0.7. The trend, tenuous as it may be, was used as the basis for our further studies. A few attempts to determine

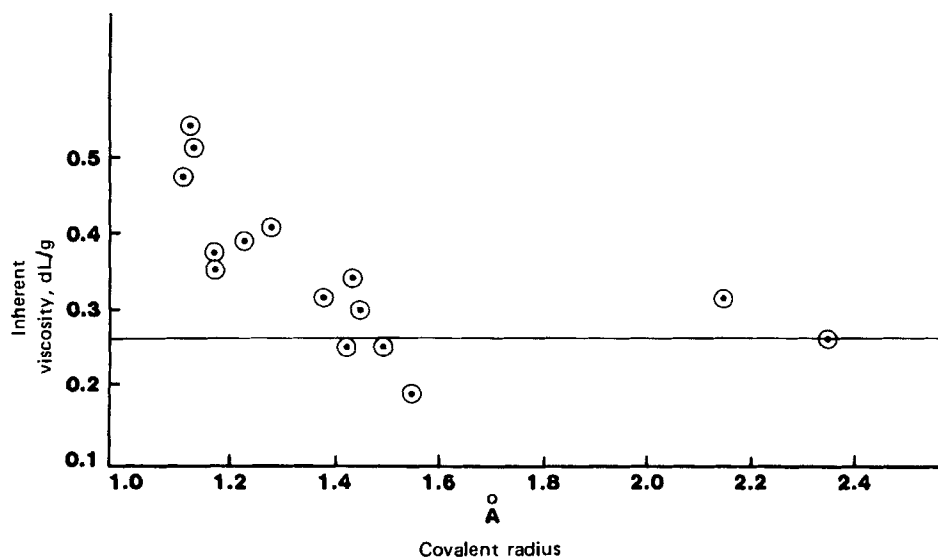


FIG. 1. Variation of inherent viscosity with catalyst metal covalent radius.

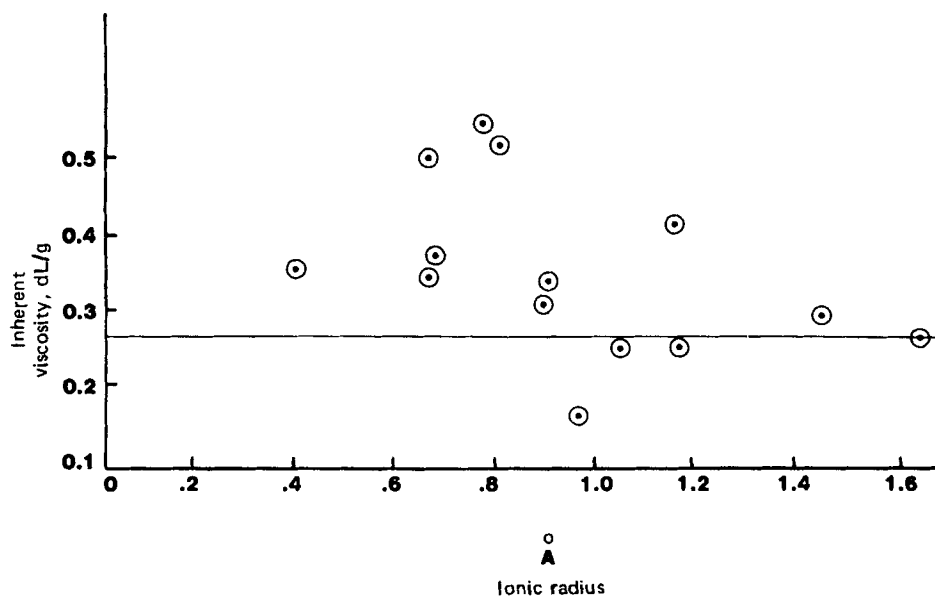


FIG. 2. Variation of inherent viscosity with catalyst metal ionic radius.

the effects of the metal salts upon the kinetics of the polycondensation were made. The data in Table 4 confirm the earlier conclusion that the levels of metal salt have essentially no effect upon the rates of endgroup disappearance or upon the molecular weight increase. While the high degree of error in these experiments precludes these experiments from being used to draw firm conclusions, they serve to add further weight to the trends seen in the screening experiments described above. The significant point that emerged from these experiments was that the nickel salts appeared to be superior catalytic materials in this polymerization system.

In view of these results, it seemed a method was needed that would maintain the active catalyst species, believed to be a transition metal phthalate, in solution with the reactants. One approach was to modify the nature of the active catalyst composition, since it was believed that the fate of the metal acetates in the presence of the phthalic acids at 200°C was to evolve acetic acid and form the insoluble metal phthalate. Due to the volatility of acetic acid, the transition metal would be present exclusively as either a diphtalate or a polymeric phthalate salt. The solubility of this salt would be expected to be extremely low, at least less than that of isophthalic acid, in the hot diphenyl ether. We therefore needed to prevent the formation of insoluble diphtalate or polymeric salt. We reasoned that this could be accomplished through either the use of a mixture of metal acetate and metal-strong acid salts which in solution should equilibrate to a mixed salt, or by *in situ* formation of the mixed salt by addition of 1 mol of a strong acid to 1 mol of the metal acetate.



The results of the experiments with mixtures of transition metal salts are summarized in Table 5. For the manganese- and cobalt-catalyzed polycondensations, the molecular weights are not significantly different from those of the acetate-catalyzed polymerizations. The nickel-catalyzed systems, however, show a marked effect of the addition of a strong-acid salt. At equivalent metal salt levels, the mixed salt systems gave inherent viscosities almost double those obtained with the simple acetate salt. Since the comparisons are made at equal molar levels of metal and the earlier data indicated that the salts of strong acids were ineffective as catalysts for transacylation, one can conclude that there is some complex of the acetate and the strong-acid salt that is responsible for the striking increase in the molecular weight. It is also apparent that the polymer molecular weights obtained are not a function of the catalyst level.

TABLE 4. Rates of Transacylation

Experiment	Catalyst (level) <sup>c</sup>	CEG, <sup>a</sup> meq/g			AEG, <sup>b</sup> meq/g				
		0 h	2 h	5 h	22 h	0 h	2 h	5 h	22 h
A	Control	676	528	356	95	616	626	322	36
B	Control	710	346	193	95	672	308	157	56
C	Mn(Ac) <sub>2</sub> (0.01)	750	285	211	92	955	294	201	62
D	Mn(Ac) <sub>2</sub> (0.10)	396	171	103	35	970	510	222	54
E	Mn(Ac) <sub>2</sub> (0.10), Ac <sub>2</sub> O (0.5)	348	35	23	8	1800	482	220	90
F	Mn(Ac) <sub>2</sub> (0.25)	237	380	229	11	1000	510	194	42
G	Ni(Ac) <sub>2</sub> (0.01)	389	610	203	55	1200	525	198	65
H	MnCl <sub>2</sub>	512	680	633	61	1730	815	530	121

<sup>a</sup>Carboxyl end groups.<sup>b</sup>Acetyl end groups.<sup>c</sup>Mole-% based on total acid charged.

TABLE 5. Effect of Mixed Salts as Polymerization Catalysts

Metal salt 1	Metal salt 2	Total mol% <sup>a</sup>	$\eta_{inh}$ , <sup>b</sup> dL/g
Mn(OAc) <sub>2</sub>	Mn(NO <sub>3</sub> ) <sub>2</sub>	0.20	0.30
Mn(OAc) <sub>2</sub>	MnCl <sub>2</sub>	0.10	0.41
Co(OAc) <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	0.10	0.45
Ni(OAc) <sub>2</sub>	NiCl <sub>2</sub>	0.10	0.45
Ni(OAc) <sub>2</sub>	NiCl <sub>2</sub>	0.02	0.80
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.02	0.82
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.04	0.68
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.08	0.48
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.10	0.78
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.20	0.43
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.40	0.62
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.60	0.73
Ni(OAc) <sub>2</sub>	Ni(ClO <sub>4</sub> ) <sub>2</sub>	0.80	0.53

<sup>a</sup>Based on total acid charged.

<sup>b</sup>Determined on 0.1% solution in 10/7 phenol/tetrachloroethane.

Whereas experiments with the metal acetates showed lower molecular weights at high catalyst levels, these mixed systems show no effect. This result is consistent with the removal of phthalic acid from the reaction by precipitation with the divalent metal acetate, but not with the mixed salt systems. This is further evidence for the solubility-maintaining effects of the strong acid salt species in the catalyst.

Similar behavior was found when the mixed salt catalyst was generated *in situ* by the addition of a strong mineral acid to the reaction mixture containing a metal acetate salt. In these experiments the mixed salt should be the same species as that generated by physically mixing the two salts. The polymerization results for these reactions were similar to those obtained by premixing the two salt components, as can be seen from the data in Table 6. The reactions seemed to proceed at about the same rate for the two systems, and the only

TABLE 6. Effect of *in situ* Formed Mixed Salts as Polymerization Catalysts

Metal acetate (mmol)	Strong acid (mmol)	Mixed salt, <sup>a</sup> mol%	$\eta_{inh}$ , <sup>a</sup> dL/g
Mn(OAc) <sub>2</sub> (0.04)	HNO <sub>3</sub> (0.04)	0.20	0.36
Mn(OAc) <sub>2</sub> (0.02)	HCl (0.02)	0.10	0.38
Co(OAc) <sub>2</sub> (0.02)	HNO <sub>3</sub> (0.02)	0.10	0.48
Ni(OAc) <sub>2</sub> (0.03)	HCl (0.03)	0.10	0.50
Ni(OAc) <sub>2</sub> (0.01)	HNO <sub>3</sub> (0.01)	0.05	0.78
Ni(OAc) <sub>2</sub> (0.04)	NHO <sub>3</sub> (0.04)	0.20	0.82
Ni(OAc) <sub>2</sub> (0.06)	HNO <sub>3</sub> (0.06)	0.30	0.73

<sup>a</sup>Based on total acid charged.

<sup>b</sup>Determined on 0.1% solution in 10/7 phenol/tetrachloroethane.

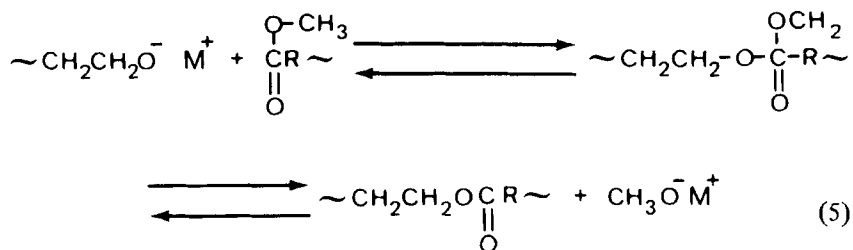
perceivable difference was that a slightly lighter colored polymer was produced when the mixed salts were generated *in situ*.

As the last step in the catalyst optimization we wanted to make certain that the catalyst components were all in solution in the reaction mixture. To this end a solution of nickel acetate and nickel nitrate in acetic anhydride was found to be very effective. The acetic anhydride proved to be an excellent solvent for the salt components and served as a drying agent, allowing the use of hydrated nickel salts for the catalyst preparation. In addition, the use of a small quantity of acetic anhydride to the polymerization reaction had previously been found to improve both the molecular weight and color of the polymer. Use of the standardized nickel salt solution also permitted addition of the catalyst by volume rather than by weight with the problems attendant to the multiple weighings and addition of small quantities of solids to a reaction.

### PROPOSED MECHANISM OF CATALYSIS

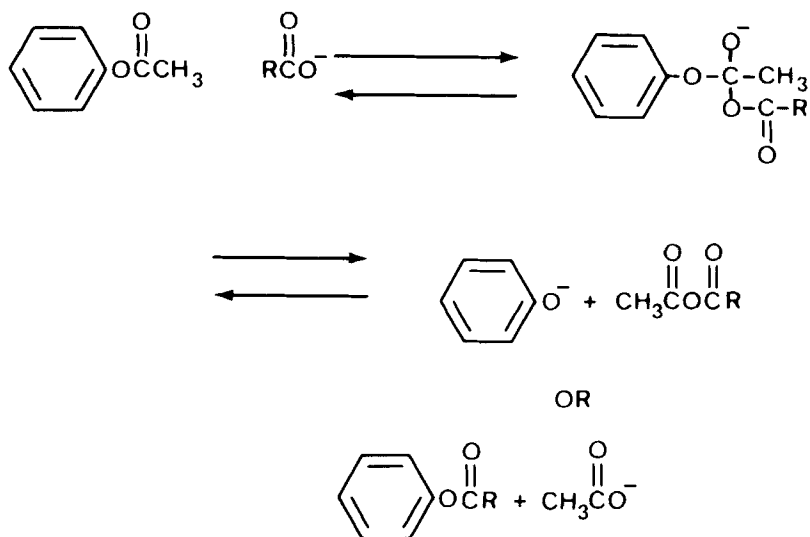
In the catalysis of the transesterification of an ester with a glycol, the first step in the preparation of polyesters by metal salts is believed to involve the formation of a metal glycolate intermediate. The glycolate ion is believed to attack the ester linkage, resulting in the formation of a new ester linkage and

the liberation of the metal alkoxide by reaction with fresh glycol, reforming the metal glycolate.

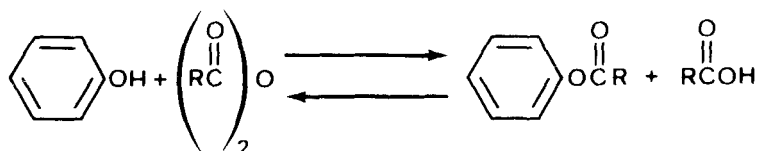
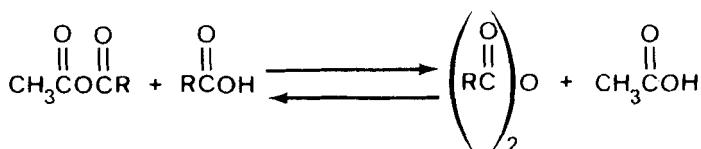
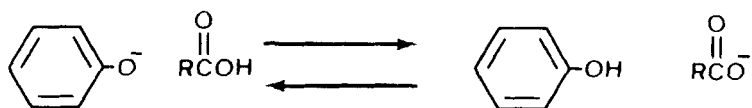


The transition state, therefore, involves an intermediate that has three oxygens associated with a carbon center. The transesterification, therefore, is the re-scrambling of the bonds to expel one of the alkoxide moieties from the intermediate.

A similar intermediate is proposed by Temin [6] to explain the course of the acidolysis of a phenyl acetate by a free acid in the presence of an alkali salt. This mechanism involves the attack of a carboxylate ion upon the phenol acetate, giving rise to a similar transition state. The transition complex can either go to the desired new ester or can decompose to a mixed anhydride which can then interchange to the simple anhydride and finally to the new ester.



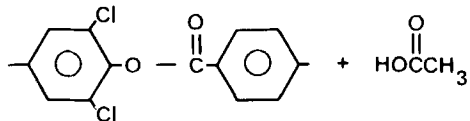
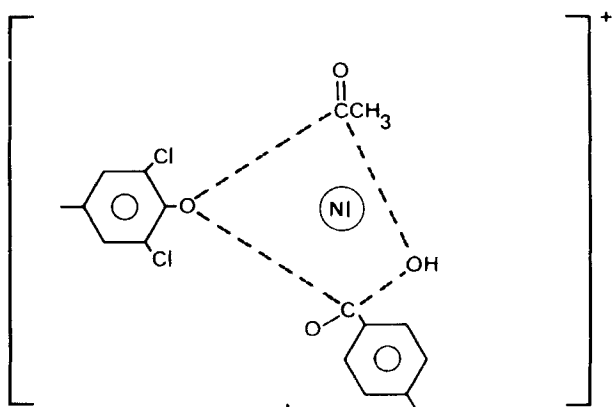
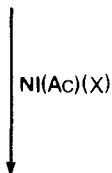
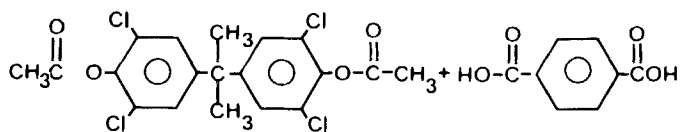




Among the features of the above reaction scheme, the transition intermediate which involves the association of the carboxylate with the ester is similar to that proposed for the interchange with glycolate. This transition state seems to agree with our results, with the exception that it does not account for the differences in activity between the various salts since the mechanism involves a free carboxylate as the attacking species, which would eliminate the effects of the cation.

Our results have led us to a slightly modified picture of the transition state, which has been useful in optimizing the process. While we have not done sufficient work to describe the catalytic complex unequivocally, we feel that our proposed structure fits our data.

It is proposed that the active catalyst species is a complex made up of the transition metal with the phenol acetate and the carboxylic acid as indicated by equation shown on the facing page. This complex is a transitory species, where the coordinated structure forms and dissociates constantly as long as there are reactants present in the system. The role of the transition metal is to provide a site for the proper orientation of the reactants in the complex. It is further anticipated that the ability of a transition metal to form an effective catalytic transition would be strongly affected by the size of the metal ion. In other words, the ability to form the complex in which all the oxygen



atoms are in the proper equivalent positions will be a function of the size of the metal ion. We feel that such an intermediate is necessary to explain the differences in effectiveness among the various metal salt catalysts.

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