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Synthesis and characterization of new bivalent tin chelate of 3-hydroxy-2-methyl-4-pyrone and its use as catalyst for polyesterification

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Summary

We describe here the synthesis of a new tin chelate $Sn(C_6H_5O_3)_2.2H_2O$. The catalytic performance of this chelate is shown for polyesterification reactions involving terephthalic acid and poliols, such as neopentylglygol and trimetilolpropane. The complex is highly active for low molecular weight (M_n = 1700 and M_w = 4500) polymer formation. IR spectra also show free OH in the polymer chain.

Introduction

Transition metal chelates using OˆO ligants, such as carboxylates, di-ketonates and quinones, have long been known to possess numerous chemically and biologically applications. For instance, quinones and their substitute derivatives have been described as antitubercular and antibacterial agents[1,2]. On the other hand, the di-ketonates and carboxylates are used for dimerization, telomerization, oxidation and oligomerization of olefins and dienes[3,4]. A quinone quelate was described as a catalyst precursor for the polymerization of dienes[5], showing high selectivity due to π electron delocalization. Extensive screening of potential catalysts for esterification has showed that Sn^{2+} is a good catalyst for polyesterification[3]. A paper of L. Nondek and J. Malek[6] has focused attention on compounds that catalyze the reaction of ethylene glycol with isophtalic acid. The tin compounds reported to have good activity in direct esterification include tin (II) oxide and tin (IV) oxides, oxalate, carboxylate and alkyl compounds. In this paper, we report on the synthesis and characterization of a novel tin quelate of 3-hydroxy-2-methyl-4-pyrone, and its use as a catalyst for polyesterification of terephatalic acid (TFA), neopentyl glycol (NPG) and trimethylolpropane (TMP).

Experimental

General Procedures

The analyses were carried out on different equipment: the calorimetric experiments were carried out on a PL-DSC 12000, the molecular weight distribution was obtained in a Polymer Laboratories GPC Data Station 4.0, the IR spectra were recorded on a BOMEM MB Series Spectrophotometer, and the elemental analyses were performed on a Perkin Elmer 2400.

Preparation of the Chelate

Reagent grade tin chloride, 3-hydroxy-2-methyl-4-pyrone and sodium hydroxide were obtained from commercial sources and were used as received without further purification. 0.2 mmol of ligant (3-hydroxy-2-methyl-4-pyrone) and 2 mmol of sodium hydroxide were dissolved in 20 mL of distilled water. To this solution, 0.1 mmol tin chloride dissolved in 20 mL of water was slowly added under continuous magnetic stirring. The mixture was left stirring at 323 K for 30 minutes and then was kept in a refrigerator overnight. The resulting precipitate was isolated by filtration, washed several times with distilled water and dried in a vacuum dessicator over silica gel. 158.63 mg (0.43 mmole, 43%) of $Sn(C_6H_5O_3)_2.2H_2O$ was obtained. This white pearl complex is soluble in dimethylsulphoxide and dimethylformamide.
IR (KBr pellets): 1602.62 (νC=O (1) - M), 1570.41 (νC=O (2) - VS), 1506.00 (νC=C (1) - VS), 1461.05 (νC=C (2) - S). Calculated for $Sn(C_6H_5O_3)_2.2H_2O$: C, 35.59 %; H, 3.48 %. Found: C, 35.50%; H, 3.52%.

Polymerization Reactions

Catalytic reactions were carried out in the reactor system, which is shaped in the form of a four neck round-bottom flask of two liters. The flask is equipped with an air-driven stirrer, a thermocouple, a nitrogen inlet tube, two adjacent partial reflux condenser, one of them charged with a packing, and the other is a steam- jacketed partial reflux condenser. A tube test receiver is installed in one of the four necks. The flask is heated by means of an electrical heating mantle. The temperature is monitored via a Pt 100 thermocouple with a temperature controller. The mantle is connected to the automatic controller. The use of a steam-jacketed partial reflux condenser helps to prevent the loss of the more volatile reactants, while allowing the efficient removal of water. This control is quite important because the loss of the reactants may alter the molecular weight and properties of the polyester. A partial condenser containing packing increases the condensation area of the condenser and physically opposes the flow of reactant vapors carried in the inert gas stream. The temperature in the top of the condensers is monitored by a thermometer. The monomers such as terephtalic acid (TFA), neopentyl glycol (NPG) and trimethylolpropane(TMP) are commercial products and were used without further purification in the proportion of 4.8: 4.2: 2.1 respectively. In a typical reaction, TMP (2.1 moles, 285.4g) and NPG (4.2moles, 436.8g) are combined into the reaction flask and heated until melting. The stirrer is turned on (0.666Kgf/cm^2). The system is heated to 140°C and TFA and tin complex are added. The temperature is increased from 150°C until 230°C during 5 hours. The temperature is maintained at 230°C. Samples (1 cm^3) are withdrawn from the reaction mixture and the variation of acid number and water content are evaluated during this period. The acid number, i.e., the total concentration of the carboxylic groups, are measured by diluting about 1.0 g of the sample to 50cm^3 DMF. The sample is heated until fusion without boiling. Then the sample is titrated with 0.1N KOH in methanol with phenolphtalein as the indicator, at room temperature. The acid number is calculated [7] by (AN=V(mL) x 56.1 x N)/P[mgKOH/g] were V= volume of titrate liquid; N= Normality of titrate liquid and P= sample mass.

Polymer characterization

Polymer products were characterized by FTIR, thermal analysis, viscosity and DSC. Molecular weights and molecular weight distributions of the polymers were determined by viscosity and gel permeation chromatography, using THF as the eluent.

Results and Discussion

The new compound is a bivalent tin complex and is an air stable thin powder. It is insoluble in water and most of the common organic solvents, being soluble only in DMF and DMSO. The FTIR study showed a shift of ligant C=O bond band to lower frequency and the disappearance of O-H bond band when the complex is formed. This result allowed us to suggest that coordination occur by both ligant oxygens, forming a 5-membered chelate ring, as shown in fig. 1 below. The CHN results indicate that the isolated compound also contains two coordinated molecules of water.

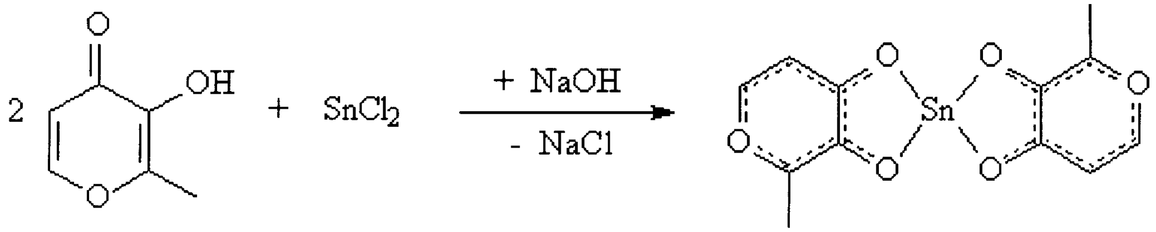

Figure 1- Tin catalyst

The above-cited tin complex showed catalytic activity for the polyesterification of TFA, NPG and TMP. Different amounts of tin catalysts were used as we can see in Table I.

Table I- Main results for polyesterification using different amounts of tin catalyst.

Entry	Catalyst Content (% in mass)	Reaction time (h,min)	AN (mgKOH/g)	Viscosity (cP)	Productivity	Water (g)
1	0.05	18.31	4.80	485	364.4	142.29
2	0.10	13.25	5.40	355	250.8	163.93
3	0.15	13.20	5.00	133	235.0	131.58
4	0.20	11.30	5.50	330	154.8	161.03
5	0.25	12.55	3.80	525	104.3	146.44
6	0.30	9.35	4.90	385	117.0	170.22

a) Productivity = (kg of polymer obtained).(g of tin)$^{-1}$.(time in hours)$^{-1}$

Water content values were between 142.3g (Entry 1) and 170.2g (Entry 6), which is less than the theoretically calculated water formation for these experimental conditions (173.9g). Probably, these differences are due to difficulties in removal of water content from the reaction medium because of its high viscosity or because of incomplete polyesterification reaction.

The reaction time has varied between 9h35min and 18h31min. By increasing the catalyst quantities we can observe a decrease in the reaction time. However, the productivity value is higher for reactions with lower catalyst content, so we can conclude that the behavior is not linear, i.e. increasing the catalyst content the reaction velocity does not increase linearly. This behavior has been already described for alkyltin catalyzed polyesterification[8]. A plausible explanation is the formation, in higher concentrations, of oligomeric tin complexes, which are less catalytic active.

The distribution of molecular weight appeared to be relatively narrow, showing M_n = 1700 and M_w = 4500, with M_w/M_n equal 2.6. It is important to note that no variation in molecular weight was observed for different catalyst concentrations. The DSC analysis indicated a Tg at 35.91°C and no crystallization peaks indicating that the samples are amorphous.

The infrared spectra allowed us to observe bands relative to ester formations ($\nu_{C=O}$ esther 1722.58 cm^{-1} and ν_{C-O-C} 1106.72 cm^{-1}) and to confirm the existence of hydroxiles groups ($\nu_{O-H\ free}$ 3514.71 cm^{-1}) all over the polymeric chain for all polymer samples.

In order to compare this new complex behavior with commercials ones, polyesterification was carried out using the well-known commercial catalyst Bu_2SnO. In the same conditions of entry 4, this catalyst achieved a productivity of 72.2, producing similar polyester (viscosity of 330 cP).

Conclusions

We have shown an efficient and simple method for the preparation of the new complex $Sn(C_6H_5O_3)_2.(H_2O)$. This new complex showed high catalytic activity for polyesterification of terephthalic acid, neopentyl glycol and trimethylolpropane.

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