Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymer-Supported Lewis Acid Catalysts. IV. Complexes of Stannic Chloride and a Functional Polymeric Carrier

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To cite this Article Ran, R. C. and Mao, G. P.(1990) 'Polymer-Supported Lewis Acid Catalysts. IV. Complexes of Stannic Chloride and a Functional Polymeric Carrier', Journal of Macromolecular Science, Part A, 27: 2, 125 — 136
To link to this Article: DOI: 10.1080/00222339009351491
URL: http://dx.doi.org/10.1080/00222339009351491

J. MACROMOL. SCI.—CHEM., A27(2), pp. 125-136 (1990)

POLYMER-SUPPORTED LEWIS ACID CATALYSTS. IV. COMPLEXES OF STANNIC CHLORIDE AND A FUNCTIONAL POLYMERIC CARRIER

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ABSTRACT

Five types of polymer carrier beads containing functional groups were synthesized by copolymerization of styrene, divinylbenzene, and a third functional monomer containing oxygen and/or nitrogen. They were combined with stannic chloride in chloroform to form five stable polymeric complexes containing 17–34% Cl, which corresponds to 1.2–2.4 mmol $SnCl_4$/g. These complexes showed good stability and high catalytic activity in many organic reactions, such as acetalation, esterification, and ketal formation. They also can be reused at least 6–8 times without losing their activity in organic reactions.

INTRODUCTION

Polymeric catalysts have been investigated by many scientists, and this has been a rapidly developing, important field of polymer science [1–4].

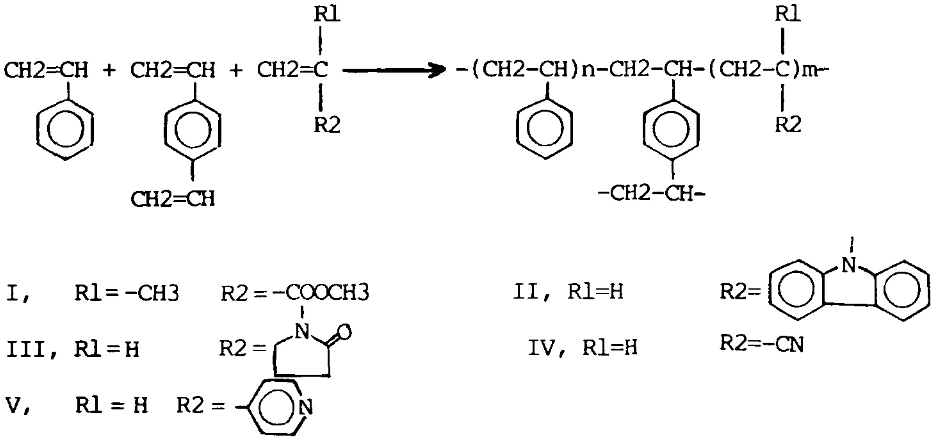
Stannic chloride is a strong Lewis acid and an important and useful catalyst in organic synthesis and polymer chemistry, but it is easily hydrolyzed in air, so that its use, storage, and separation from reaction mixtures are inconvenient and difficult. For these reasons we prepared a polystyrene-supported stannic chloride catalyst [5] which showed good catalytic activity in organic reactions such as esterification, acetalation, ketal formation, and etherification, but its activity in repeated use was poor. The work reported here was undertaken to improve the reusability of the polymer complex.

EXPERIMENTAL

Materials

All monomers and solvents were purified by standard methods. The stannic chloride was an AR reagent used without further purification. The internal standard used in GC was a standard reagent.

Preparation of Polymeric Carriers (Scheme 1).



SCHEME 1. Synthesis of polymeric carriers.

The polymeric carriers were synthesized by suspension copolymerization of styrene, divinylbenzene (DVB), and a functional monomer (see Table 1). The 20–100 mesh beads were used as carrier in the polymer-supported catalysts. Elemental analysis of the copolymer beads gave the amount of functional monomer in each carrier polymer.

TABLE 1. Amount of Lewis Acid in Polymer-Supported Stannic Chloride Complex Catalyst, and Composition of the Polymeric Carriers

Catalyst	Cl, %	$SnCl_4$ mmol/g	N, %	Content of Functional Group[a] mol%	Content of Functional Group[a] mmol/g
PMMA-$SnCl_4$	20.5	1.44		19.0	1.90
PVCZ-$SnCl_4$	20.8	1.47	1.75	14.6	1.25
PVPr-$SnCl_4$	17.7	1.24	1.73	13.0	1.23
PAN-$SnCl_4$	21.5	1.51	3.65	23.9	2.60
PVPd-$SnCl_4$	34.0	2.40	4.7	35.0	3.35
PS-$SnCl_4$	10.8	0.76			

[a] Functional monomer: methyl methacrylate (MMA), *N*-vinylcarbazole (VCZ), *N*-vinylpyrrolidone (VPr), acrylonitrile (AN), and 4-vinylpyridine (VPd), respectively. PS: polystyrene.

Preparation of Polymer-Supported Catalysts

A 20-g quantity of the carrier beads containing functional groups (see Table 1) swelled when 100 mL chloroform was stirred with 8 mL stannic chloride for 48 h at room temperature. The color of the beads changed to red or green. The reaction mixture was filtered and washed 5 times with 300 mL chloroform, and then twice with 100 mL acetone. The complex beads were dried under vacuum for 72 h at 40°C.

Determination of the Quantity of Stannic Chloride and the Acidity

The chlorine contents of the complex beads were determined volumetrically by a method described earlier [5]. The amount of stannic chloride in the complexes was calculated from the chlorine content.

The complex beads were hydrolyzed in acetone–water solutions and the pH was determined (Digital pH/temperature meter 3055) at 25°C.

Ultraviolet and Infrared Spectral Analysis

Uncrosslinked copolymers of the same composition as the crosslinked carriers were dissolved in chloroform or dimethylsulfoxide (DMSO), and UV spectra were obtained with an ultraviolet-visible spectrophotometer

(Shimadzu UV-250). Infrared spectra of the same samples were determined with a IR spectrophotometer (Shimadzu IR-408).

Test of Catalytic Activity in Organic Reactions

In the presence of the polymer-supported stannic chloride complex catalysts, organic reactions such as esterification, acetalation, ketal formation, and etherification were carried out in benzene under reflux with a Dean-Stark trap for 2 h at 85–95°C. Yields of these reactions were determined by gas chromatography (SP 2307) with an internal standard.

RESULTS AND DISCUSSIONS

Synthesis of Polymeric Carriers and Catalysts

The polymeric carriers containing functional groups were synthesized by the method shown in Scheme 1. Their properties and those of the polymer-supported stannic chloride complex catalysts are shown in Table 1.

Hydrolysis of the Complexes

Figure 1 shows that the acidity due to hydrolysis of these polymeric complexes in 60:40 acetone:water increases with time, and reaches equilibrium in 1–2 h. This confirms that some stannic chloride is present in these polymeric complexes.

UV and IR Spectral Analysis

All the complexes displayed different colors during the preparation. This is an essential characteristic of the complexes.

Three complexes, PVPr-$SnCl_4$, PAN-$SnCl_4$, and PVPD-$SnCl_4$, are soluble in some polar solvents, such as dimenthylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF). It is clear that the polarity of these three complexes is stronger than that of the other two, which are soluble in chloroform.

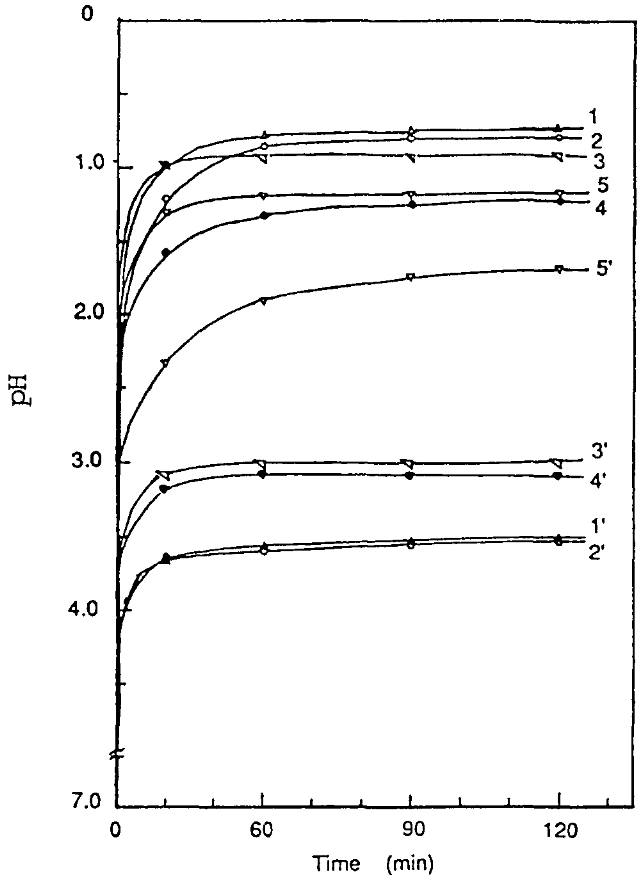


FIG. 1. Hydrolysis of pH of polymer-supported stannic chloride complex. 1-5, pH of polymer-supported SnCl$_4$ complex in 60:40 acetone-water solution (4% w/v). 1'-5', pH of used catalysts and stored in reaction mixture for 15 days, 1, 1', PAN-SlCl$_4$; 2, 2', PMMA-SnCl$_4$; 3, 3', PVCZ-SnCl$_4$; 4, 4', PVPr-SnCl$_4$; 5, 5', PVPd-SnCl$_4$.

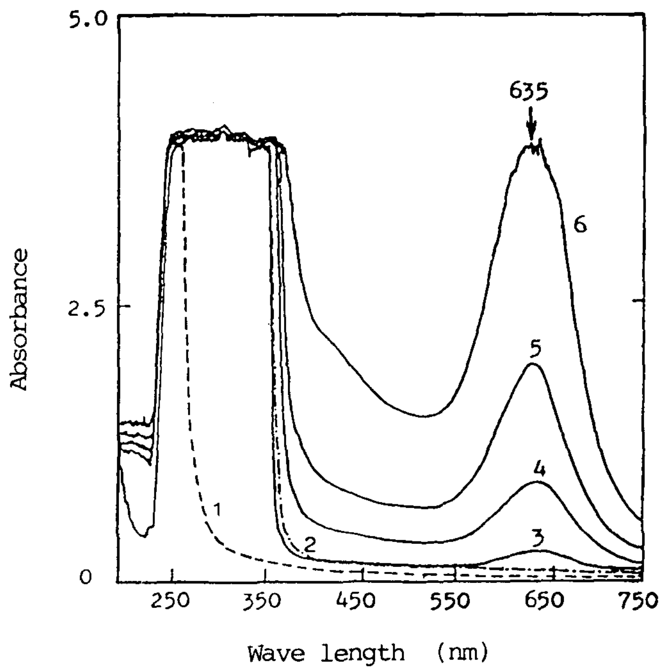
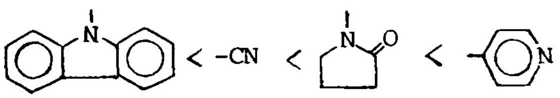


FIG. 2. UV spectra of PVCZ-$SnCl_4$ complexes. 1, $SnCl_4$; 2, PVCZ; 3-6, PVCZ-$SnCl_4$ complex, 1, 2, 2.5, and 5% in chloroform, respectively.

One or two new bands appeared in the UV spectra of these complexes in solution, but no new UV bands appeared in those of polystyrene-stannic chloride complex [5]. For example, a new band appeared at 635 nm for the PVCZ-$SnCl_4$ complex (see Fig. 2), and at 340 nm for the PVPr-$SnCl_4$ complex (see Fig. 3), respectively.

The Lewis basicity of the functional groups in these polymeric carriers is different, which results in different structures of the complexes. The Lewis basicity of the functional groups follows the following order:



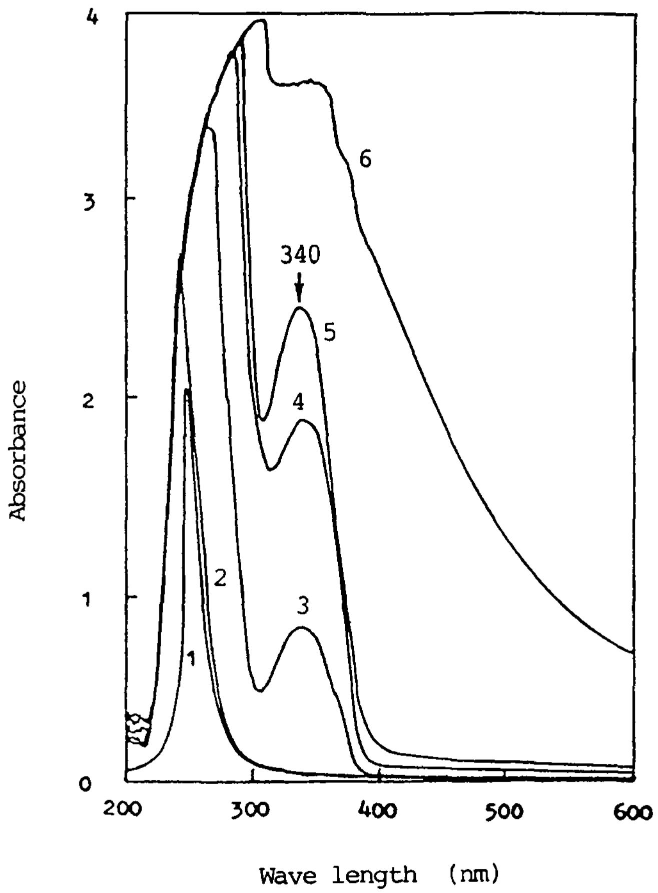
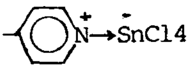


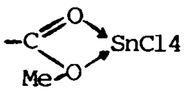
FIG. 3. UV spectra of PVPr-SnCl$_4$ complexes. 1, SnCl$_4$; 2, PVPr; 3–6, PVPr-SnCl$_4$ complex, 1, 2, 2.5, and 5% in DMSO, respectively.

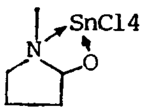
The pyridyl and nitrile group, with the stronger Lewis basicity, formed stable coordination complexes with polar *n*→*p* type coordination bond between stannic chloride and nitrogen:

-CN→SnCl4



The pyrrolidinyl and methyl ester site with three-atom conjugate systems and unshared electron pairs can form stable polar coordination complexes with four atoms:





However, the carbazolyl system is a large aromatic conjugate system with 13 atoms, no unshared electron, and weak Lewis basicity. Thus it forms a stable *π*→*p* type large coordination complex with stannic chloride, and a very strong band appears at 635 nm (Fig. 2).

It is clear that the formation of these complexes between stannic chloride and polymeric carriers results in stabilization of these polymer-supported stannic chloride complex catalysts.

The IR spectra of these polymer-supported stannic chloride complexes were very different from those of their polymer carriers, respectively. For example, the IR spectrum of the polyacrylonitrile (PAN) carrier exhibits the typical $-C\equiv N$ group absorption at 2225 cm^{-1}. In the IR spectrum of the polymeric complex with stannic chloride (PAN-$SnCl_4$), however, this absorption band is not present. The absorption bands at 2700–3500 cm^{-1}, which are due to the complex of carbonyl with stannic chloride, and the bands at 1200–650 cm^{-1} also showed obvious differences between the polymer carrier (PAN) and the polymer complex (PAN-$SnCl_4$).

In summary, the UV and IR spectra indicate that stable complexes are formed between polymeric carriers containing functional groups and stannic chloride, and that the presence of oxygen and/or nitrogen resulted in stabilization of these complexes. Hence, these polymer-supported stannic chloride complex catalysts are very stable. Even after storage for 2 years, they did not lose their catalytic activity and were by far more stable than that of the polystyrene-stannic chloride complex catalyst (PS-$SnCl_4$) [5].

Catalytic Activity in Organic Reactions

(1) Catalytic Esterification

Table 2 shows that the catalytic activity of the five complex catalysts for esterification was good and never less than that of the plain polystyrene-stannic chloride complex catalyst (PS-$SnCl_4$) [5] in the same reactions.

(2) Catalytic Acetalation

Table 3 show that these complex catalysts show good catalytic activity for the acetalation reaction, and the yields were in keeping with the Hammett substituent constants.

(3) Catalytic Ketal Formation

Table 4 shows that these catalysts exhibit very good catalytic activity in ketal formation reactions and that the catalytic activity was better than

TABLE 2. Yields (%) of Catalytic Esterification of Carboxylic Acids with Butyl Alcohol[a]

Catalyst	R in Acid[c] $-CH_3$	 $-C_2H_5$	 Phenyl
PMMA-$SnCl_4$	97	84	72
PVCZ-$SnCl_4$	100	80	73
PVPr-$SnCl_4$	83	85	70
PAN-$SnCl_4$	100	96	72
PVPd-$SnCl_4$	85	95	58
PS-$SnCl_4$	74	100	22
PS-$AlCl_3$[b]	30	70	22.9
PS beads	4	7	0

[a] Reaction conditions: acid/alcohol = 1/2 (mol/mol), reaction time 2 h, yields measured by GLC.

[b] PS-$AlCl_3$: polystyrene-$AlCl_3$ complex [6, 7].

[c] $R-COOH + n\text{-}BuOH \rightarrow RCOOBu + H_2O$.

TABLE 3. Yields (%) of Catalytic Acetalation of Substituted Benzaldehyde with *n*-Butyl Alcohol[a]

	R in aldehyde[b]							
Catalyst	H	*o*-NO_2	*p*-NO_2	*m*-NO_2	*p*-Cl	*p*-OH	*o*-OH	*o*-OCH_3
PMMA-$SnCl_4$	69	76	71	90	47	46	37	53
PVCZ-$SnCl_4$	57	54	61	74	55	39	33	46
PVPr-$SnCl_4$	61	53	61	74	63	39	33	51
PAN-$SnCl_4$	57	70	64	60	55	34	31	48
PVPd-$SnCl_4$	40	69	93	76	62	40	38	22
PS-$SnCl_4$	67	94	90	86	81	18	15	
PS-$AlCl_3$[c]	21	62	48					
PS beads	5		8			0		

[a] Reaction conditions: Alcohol/aldehyde = 2/1 (mol/mol), reaction time 2 h, yields measured by GLC.

[b]

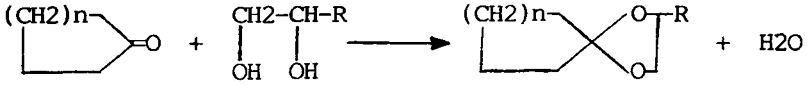
[c] PS-$AlCl_3$: polystyrene-aluminum trichloride complex [6, 7].

TABLE 4. Yields (%) of Catalytic Ketal Formation[a]

R in alcohol:[b]	R = H			R = CH_3		
n[c]	1	2	3	1	2	3
PMMA-$SnCl_4$	60	100	90	52	100	96
PVCZ-$SnCl_4$	64	100	91	21	100	56
PVPr-$SnCl_4$	57	100	85	31	100	90
PAN-SnC14	87	100	94	26	100	87
PVPd-$SnCl_4$	71	100	92	31	100	77
PS-$SnCl_4$	72	96	65			

[a] Reaction conditions: Alcohol/ketone = 1/1 (mol/mol), reaction time 2 h, yields measured by GLC.

[b]



[c] Cyclopentanone (*n* = 1), cyclohexanone (*n* = 2), cyclophetanone, (*n* = 3), respectively.

that of the plain polystyrene-stannic chloride catalyst (PS-$SnCl_4$) in the same reactions [5]. Moreover, in the ketal formation of cycloaliphatic ketones with 5–7 membered rings with ethylene glycol and propylene glycol, the yield was the highest for cyclohexanone.

Reuse of the Catalysts

The reuse properties of the complex catalysts in the ketal formation reaction of cyclohexanone with ethylene glycol were studied (Table 5). It is clear that the loss of catalytic activity and repeated use was far less for the copolymer catalyst than for polystyrene-stannic chloride [5]. Specifically, it was found that the yield was not lowered at all and remained 100% even after the catalyst PVPd-$SnCl_4$ had been reused eight times. Because there is a strong polar bond between the pyridinyl of PVPd and stannic chloride, the polymeric complex PVPd-$SnCl_4$ is very stable and can be reused many times without loss of catalytic activity. Thus these stannic chloride catalysts based on the new polymer carriers that contain functional groups with unshared electron pairs of nitrogen and/or oxygen atoms show not only good catalytic activity, but also very good stability, which is very important for industrial applications.

TABLE 5. Yields (%) of Reuse in Ketal Formation of Cyclohexanone with Ethylene Glycol[a]

	Reuse Times							
Catalyst	1	2	3	4	5	6	7	8
PMMA-$SnCl_4$	100	100	100	95	77	68		
PVCZ-$SnCl_4$	100	100	95	100	72			
PVPr-$SnCl_4$	100	100	100	83	75	64		
PAN-$SnCl_4$	100	100	100	97	75	72		
PVPd-$SnCl_4$	100	100	100	100	100	100	100	100
PS-$SnCl_4$	100	55	20	10				

[a] Reaction conditions: 1 g catalyst reused in the reaction, reaction time 1 h in each reaction, yield measured by GLC.

CONCLUSIONS

The five crosslinked styrene functional copolymer carrier beads containing methyl methacrylate (MMA), *N*-vinylcarbazole (VCZ), *N*-vinylpyrrolidone (VPr), acrylonitrile (AN), or 4-vinylpyridine (VPd), respectively, were synthesized and combined with stannic chloride to form very stable polymer-supported Lewis acid complex catalysts. These complexes exhibited good catalytic activity in many organic reactions, such as esterification, acetalation, and ketal formation. They can also be reused many times without losing their catalytic activity. Their stability was much better than that of plain polystyrene–stannic chloride complex catalyst [5]. The PVPd-$SnCl_4$ complex catalyst showed the best stability.

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Received November 7, 1988
Revision received January 20, 1989