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### Polymer-Supported Lewis Acid Catalysts. III.

### Diphenylaminomethylpolystyrene-Titanium Tetrachloride Complex

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## POLYMER-SUPPORTED LEWIS ACID CATALYSTS. III. DIPHENYLAMINOMETHYLPOLYSTYRENE-TITANIUM TETRACHLORIDE COMPLEX

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### ABSTRACT

A polymer pearl carrier, diphenylaminomethylpolystyrene, was synthesized by the reaction of chloromethylated polystyrene beads (4% DVB) with diphenylamine and was combined with titanium tetrachloride in chloroform to form a very stable complex containing 24.38% Cl (equivalent to 1.72 mmol  $\text{TiCl}_4$ /g complex beads). The complex showed good catalytic activity in organic reactions such as esterification, acetalation, and ketal formation. The catalyst can be reused at least eight times without losing its activity.

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## INTRODUCTION

Polymeric catalyst and polymer-supported metal complex catalyst have been studied by many researchers, and this has been one of the important and rapidly developing fields of polymer science [1-8].

It is well known that titanium tetrachloride is a strong Lewis acid, and it also is an important catalyst in organic synthesis reactions and polymer chemistry. However, it easily hydrolyzes in air, so that use, storage, and separation from the reaction mixtures are inconvenient. We have prepared a complex of titanium tetrachloride with polystyrene [9]. The complex showed good catalytic activity in organic reactions such as esterification, acetalation, and ketal formation, but its ability to be reused was poor. In order to improve the stability of the complex, we synthesized a new polymer carrier containing diphenylamine groups and combined it with titanium tetrachloride to form a very stable complex. The complex not only showed good stability, but also good catalytic activity in the same organic reactions.

## EXPERIMENTAL

### Synthesis of the Polymer Carrier

Chloromethylated styrene-divinylbenzene (4%) copolymer beads (30 g, Shanghai 711, 3.2 mmol Cl/g, 16-50 mesh size) swollen in 100 mL chloroform were added to 200 mL of a chloroform solution of diphenylamine (24.2 g, 0.144 mol). After stirring for 24 h at 50°C, pyridine (10 mL) was added to the mixture, and then it was stirred for a further 2 h. After filtration, the resin beads were washed with 300 mL THF, followed by 300 mL water and 200 mL acetone, and then dried under vacuum for 72 h.

Elemental analysis of the polymer carrier gave 81.55% C and 4.02% N.

### Preparation of the Polymer-Supported Catalyst

The carrier beads of crosslinked polystyrene containing diphenylaminomethyl groups, diphenylaminomethylpolystyrene (PBDA) (25 g), swelled by 100 mL chloroform were stirred with 10 mL titanium tetrachloride for 6 h at room temperature, and the beads became emerald green. After cooling to 0-5°C, the mixture was filtered and washed with 300 mL chloroform and then with 100 mL acetone. The complex was dried under vacuum for 72 h, giving green beads.

### Determination of the Quantity of $\text{TiCl}_4$ Complexed

The complex samples were decomposed by burning in an oxygen bottle. The chlorine content was determined volumetrically. The amount of  $\text{TiCl}_4$  complexed with polymer carrier was calculated from the chlorine content.

### Determination of the Acidity of the Complex

The pH of the acetone-water solutions obtained by hydrolyzing the pearl complex samples in acetone-water were determined at  $25^\circ\text{C}$  with a pH meter (digital pH/temperature meter 3055).

### Ultraviolet and Infrared Spectral Analysis

UV spectra of the model compound benzyldiphenylamine complexed with  $\text{TiCl}_4$  in chloroform (containing 5%  $\text{TiCl}_4$ ) were obtained with an ultraviolet/visible spectrophotometer (Shimadzu UV-250). The infrared spectra of the same solution were determined with an IR spectrophotometer (Shimadzu IR-408).

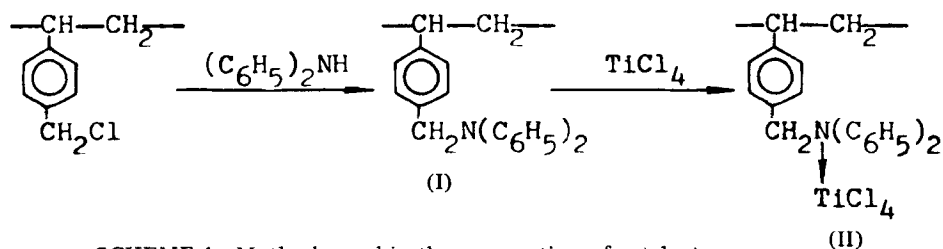
### Test of Catalytic Activity in Organic Reactions

Esterification, acetalation, ketal formation, and etherification were carried out in benzene, using the polymer-supported Lewis acid catalyst of diphenylaminomethylpolystyrene-titanium tetrachloride complex (PBDA- $\text{TiCl}_4$ ). It was refluxed, using a Dean-Stark trap, for 2 h at  $85\text{--}95^\circ\text{C}$ . Yields of these reactions were determined by gas chromatography (SP 2307 type) against an internal standard. For example, propionic acid (7.4 g, 0.1 mol), *n*-butanol (14.8 g, 0.2 mol), benzene (50 mL), and the PBDA- $\text{TiCl}_4$  complex catalyst beads (1.0 g) were allowed to react in a 100-mL flask with a Dean-Stark trap and a condenser. The mixture was heated under reflux for 2 h. The reaction solution was analyzed by GLC against chlorobenzene as an internal standard. The amount of *n*-butyl propionate and the residual *n*-butanol were determined relative to the peak area of the internal standard.

## RESULTS AND DISCUSSION

### Preparation of Polymer Carrier and Catalyst

The crosslinked polymeric analog of benzyldiphenylamine (I) was synthesized by reaction of the chloromethylated polystyrene resin with diphenyl-



Scheme 1. Methods used in the preparation of catalyst.

amine (Scheme 1). Elemental analyses of the product, diphenylaminomethylpolystyrene (I), found 4.02% N, equivalent to 2.82 mmol benzyldiphenylamine groups/g beads. Yield of the reaction was 98.6%, indicating that it proceeded nearly to completion with typically only a small amount of residual chlorine (i.e., <0.6%) remaining on the polymer carrier.

The polymer-supported Lewis acid complex catalyst diphenylaminomethylpolystyrene-titanium tetrachloride complex (PBDA-TiCl<sub>4</sub>) was prepared by the reaction of the polymer carrier (I) with titanium tetrachloride in chloroform (Scheme 1). The chlorine content of the PBDA-TiCl<sub>4</sub> complex (II) was 24.38%, equivalent to 1.72 mmol TiCl<sub>4</sub>/g of complex beads, and the content of nitrogen was 2.42%, equivalent to 1.71 mmol benzyldiphenylamine groups/g of complex beads.

#### Acidity of the Solution Obtained on Hydrolysis of PBDA-TiCl<sub>4</sub>

The pH of an acetone-water solution (60%) containing PBDA-TiCl<sub>4</sub> complex beads shown in Fig. 1, which shows that the acidity due to hydrolysis of the complexed TiCl<sub>4</sub> reached equilibrium in 2 h. Thus it is clear that some TiCl<sub>4</sub> is present in the complex.

#### UV and IR Spectral Analysis

The UV spectra of the solution of a model compound, benzyldiphenylamine (BDA), and its complex with TiCl<sub>4</sub> (BDA-TiCl<sub>4</sub>) are shown in Fig. 2. The absorption of the BDA-TiCl<sub>4</sub> complex in chloroform at lower concentration was the same as that of TiCl<sub>4</sub> plus BDA; but when the concentration of the BDA-TiCl<sub>4</sub> complex was increased, two new absorption bands at 480 and 870 nm appeared (see Fig. 2). Thus, it appears that formation of the complex of BDA with TiCl<sub>4</sub> led to the appearance of the two new absorption bands,

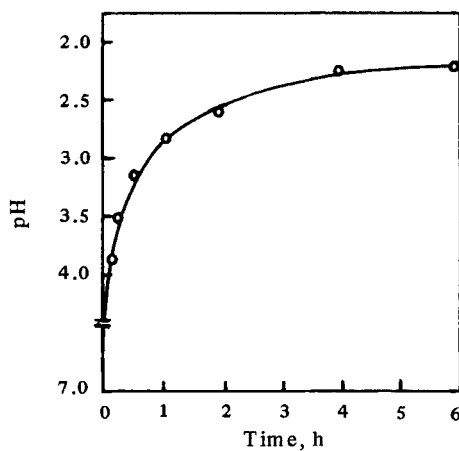


FIG. 1. Change of the pH of 50 mL acetone-water solution (60%) containing 2 g PBDA-TiCl<sub>4</sub> with time.

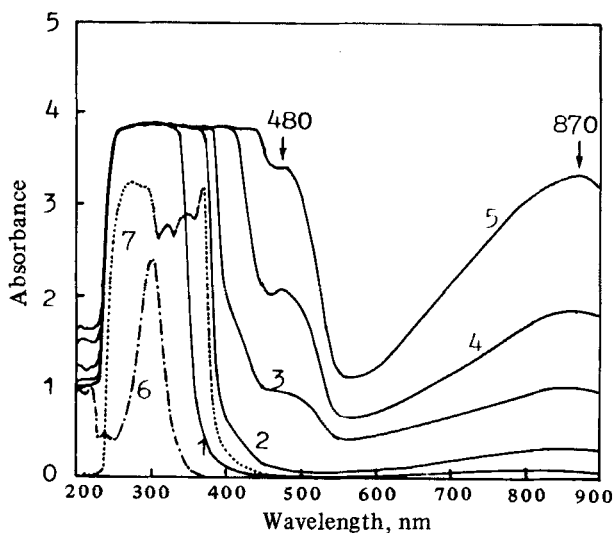


FIG. 2. UV spectra of BDA-TiCl<sub>4</sub> and reference compounds in chloroform. BDA-TiCl<sub>4</sub> concentrations: 1, 0.5%; 2, 1%; 3, 1.25%; 4, 2.5%; 5, 5%. Controls: 6, BDA; 7, TiCl<sub>4</sub>.

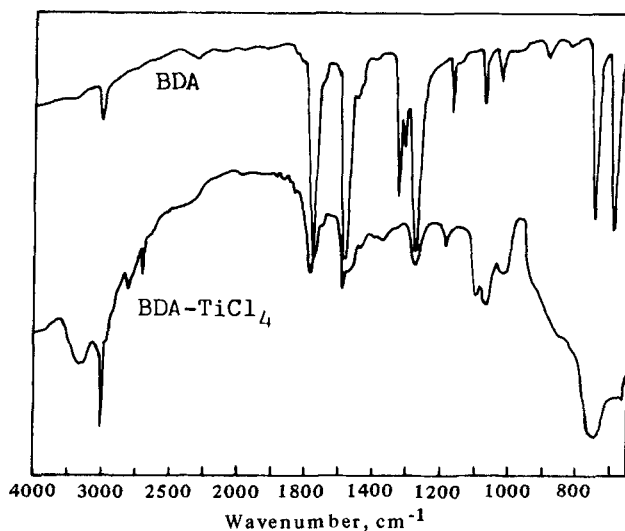


FIG. 3. IR spectra of BDA-TiCl<sub>4</sub> and BDA.

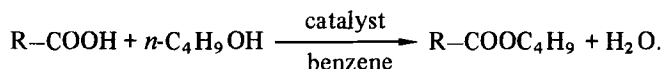
especially that at 870 nm. This effect would also stabilize the TiCl<sub>4</sub> complex with the polymer carrier containing BDA groups.

The obvious differences between the IR spectra of the BDA-TiCl<sub>4</sub> complex and BDA carrier (Fig. 3) were at 2800-3500 cm<sup>-1</sup> and at 650-800 cm<sup>-1</sup>, and especially, the characteristic absorption band of tertiary amine at 1310 cm<sup>-1</sup> was absent in the IR spectra of the BDA-TiCl<sub>4</sub> complex. Evidently, the tertiary amine in the polymer carrier (I) combined with TiCl<sub>4</sub> to form a polar-bonded complex (II). For this reason the PBDA-TiCl<sub>4</sub> complex (II) is very stable; even after over 2 years of storage, the complex catalyst did not lose its catalytic activity.

## Results of Catalytic Activity on Organic Reactions

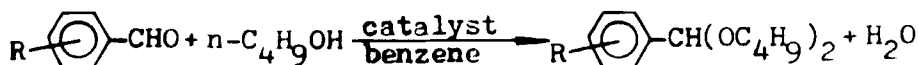
### (1) Results of Catalytic Esterification

Results of esterification of carboxylic acids with *n*-butanol catalyzed by the polymer-supported catalyst PBDA-TiCl<sub>4</sub> in Table 1 show that the catalytic activity of the PBDA-TiCl<sub>4</sub> complex was higher than that of the polymer-supported catalyst polystyrene-titanium tetrachloride complex (PS-TiCl<sub>4</sub>) [9]



## (2) Results of Catalytic Acetalation

The results in Table 2 make it evident that the polymer-supported Lewis acid catalyst PBDA-TiCl<sub>4</sub> complex exhibited good catalytic activity in the acetalation of substituted benzaldehydes with *n*-butanol and that the yields were in accord with the Hammett substituent constants.

TABLE 1. Results of Catalytic Esterification<sup>a</sup>

R in R-COOH	Catalyst	Mole ratio, acid/alcohol	Reaction time, h	Yield, %
-CH <sub>3</sub>	A	1:2	2	100
	B	1:2	2	53
	C	1:2	24	30
-CH <sub>2</sub> CH <sub>3</sub>	A	1:2	2	100
	B	1:2	2	80
	C	1:2	2	70
	D	1:2	5	9
-C <sub>6</sub> H <sub>5</sub>	A	1:5	2	70
	B	1:5	2	26
	C	1:20	5	22.9
	D	1:5	5	0

<sup>a</sup>Catalyst: A, PBDA-TiCl<sub>4</sub>; B, PS-TiCl<sub>4</sub> [9]; C, PS-AlCl<sub>3</sub> [8]; D, PBA carrier. Yields were determined by gas chromatography with chlorobenzene as internal standard.



TABLE 2. Results of Catalytic Acetalation<sup>a</sup>

R in R-C <sub>6</sub> H <sub>4</sub> CHO	Catalyst	Reaction time, h	Yield, %
H	A	2	54
	B	2	62
	C	2.5	21
	D	2	6
<i>o</i> -NO <sub>2</sub>	A	2	94
	B	2	87
	C	18	62
<i>m</i> -NO <sub>2</sub>	A	2	89
	B	2	96
	C	4	20
<i>p</i> -NO <sub>2</sub>	A	2	95
	B	2	87
	C	24	48
<i>o</i> -OH	A	2	26
	B	2	24
<i>p</i> -OH	A	2	23
	B	2	22
<i>m</i> -Cl	A	2	68
	B	2	73
<i>o</i> -OCH <sub>3</sub>	A	2	19

<sup>a</sup>Catalyst: A, PBDA-TiCl<sub>4</sub>; B, PS-TiCl<sub>4</sub> [9]; C, PS-AlCl<sub>3</sub> [8]; PBDA. Mole ratios (aldehyde/alcohol) were 1:4 in all reactions catalyzed by PBDA-TiCl<sub>4</sub>. Yields were determined by gas chromatography with butyl acetate as internal standard.

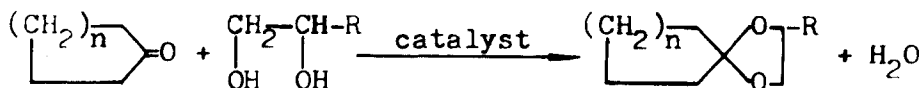
TABLE 3. Results of Catalytic Ketal Formation<sup>a</sup>

Catalyst	R in Alcohol	<i>n</i> in Ketone	Reaction time, h	Yield, %
PBDA-TiCl <sub>4</sub>	-H	1	2	83
		2	2	100
		3	2	91
	-CH <sub>3</sub>	1	2	54
		2	2	100
		3	2	87
PS-TiCl <sub>4</sub> [9]	-H	1	2	87
		2	2	99
		3	2	86
	-CH <sub>3</sub>	1	2	28
		2	2	44
		3	2	24

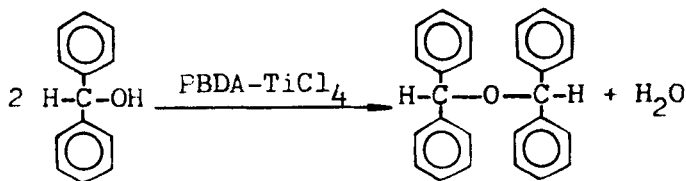
<sup>a</sup>Yields were determined by gas chromatography with *n*-butanol as internal standard. Mole ratio (ketone/alcohol) was 1:1 in all reactions.

### (3) Results of Catalytic Ketal Formation

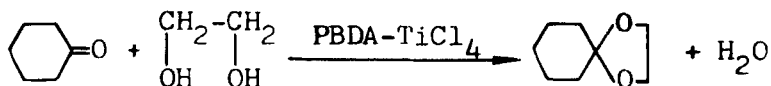
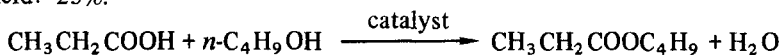
The results in Table 3 indicate that the polymer-supported Lewis acid catalyst PBDA-TiCl<sub>4</sub> complex showed very good catalytic activity in ketal formation, which was higher than that of the polymer-supported Lewis acid catalyst PS-TiCl<sub>4</sub> complex [9]. Furthermore, the yields of ketal formation of cyclohexanone with ethylene glycol and propylene glycol were the highest among those of the cycloaliphatic ketones with 5-7 membered rings.



## (4) Catalytic Etherification and Reuse of the Catalyst



Yield: 25%.



Results for esterification of propionic acid with *n*-butanol and for ketal formation of cyclohexanone with ethylene glycol catalyzed by previously used polymer-supported Lewis acid catalyst PBDA-TiCl<sub>4</sub> complex in Tables 4 and 5 show that reuse capability of the PBDA-TiCl<sub>4</sub> complex catalyst was better than that of the PS-TiCl<sub>4</sub> complex catalyst [9], and that it was better for ketal formation than for esterification. In the ketal formation of cyclohexanone with ethylene glycol, the yields of the reactions decreased only slightly when the catalyst PBDA-TiCl<sub>4</sub> complex had been reused eight times.

TABLE 4. Reuse of the Same Catalyst for Esterification<sup>a</sup>

Times of reuse	1	2	3	4	5	6	7	8
Yield, %: PS-TiCl <sub>4</sub> [9]	80	65	55.6	45.8	37			
PBDA-TiCl <sub>4</sub>	100	92	85	80	72	59	51	45

<sup>a</sup>Reaction condition: 0.1 mol propionic acid, 0.2 mol *n*-butanol, 1.5 g polymer-supported Lewis acid catalyst beads, 50 mL benzene, reaction time 1 h. Yields were determined by GLC.

TABLE 5. Reuse of PBDA-TiCl<sub>4</sub> Complex for Ketal Formation<sup>a</sup>

Times of reuse	1	2	3	4	5	6	7	8
Yield, %	100	100	100	100	100	97	93	90

<sup>a</sup>Reaction condition: 0.1 mol cyclohexanone, 0.1 mol ethylene glycol, 1.5 g PBDA-TiCl<sub>4</sub> complex beads, 50 mL benzene, reaction time 1 h. Yields were determined by GLC.

## CONCLUSIONS

The new polymer carrier containing diphenylamine groups, diphenylaminomethylpolystyrene (PBDA), was synthesized and could be combined with titanium tetrachloride to form a very stable complex PBDA-TiCl<sub>4</sub>. The complex catalyst not only showed good stability, but also good catalytic activity in many organic reactions. Polymer-supported Lewis acid catalysts are well suited for industrial production.

## REFERENCES

- [1] E. M. Fettes, *Chemical Reactions on Polymers*, Wiley (Interscience), New York, 1964.
- [2] P. Hodge and D. C. Sherrington, *Polymer-Supported Reactions in Organic Chemistry*, Wiley (Interscience), New York, 1980.
- [3] G. O. Evans, C. U. Pittman Jr., R. Mcmillan, R. T. Beach, and R. Jones, *J. Organomet. Chem.*, **67**, 295 (1974).
- [4] C. U. Pittman Jr., L. R. Smith, and R. M. Hanes, *J. Am. Chem. Soc.*, **97**(7), 1742 (1975).
- [5] C. U. Pittman Jr. and L. R. Smith, *Ibid.*, **97**(7), 1749 (1975).
- [6] N. L. Bauld and D. J. Bellville, U.S. Patent 4,503,195 (1985).
- [7] D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**(26), 9284 (1972).
- [8] E. C. Blossye, M. L. Turner, and D. C. Neckers, *Tetrahedron Lett.*, **21**, 1823 (1973); *J. Org. Chem.*, **40**, 959 (1975).
- [9] Ran Ruicheng, Jiang Shuojian, and Shen Ji, *J. Appl. Chem.*, **2**(1), 29 (1985); *Chem. Abstr.*, **103**(4), 27939v (1985).

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