

Polymer Supported Reagents. III. Kinetic Study of Synthesizing *n*-Octylacetate Using Insoluble Titanium Tetrachloride

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ABSTRACT: Insoluble poly(4-vinylpyridine-*co*-styrene) beads are prepared using divinylbenzene as the crosslinking agent. These polymer beads are converted into poly(4-vinylpyridine-*N*-oxide) (PVPNO) under peracetic acid conditions. The resulting polymer is functionalized with titanium tetrachloride (TiCl_4) to afford the corresponding PVPNO- TiCl_4 complex. This complex shows good catalytic activity for esterification reactions. The kinetics of formation of *n*-octylacetate from acetic acid and *n*-octanol is reported. The effects of stirring speed, reactant concentration, catalyst amount, percent crosslinking, particle size, and temperature on the conversion is investigated. The rate constants are found to increase with an increase in the stirring speed, concentration of *n*-octanol, catalyst amount, and temperature and decrease with an increasing percentage of crosslinking and the mesh size of the polymer beads. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2075–2080, 2000

Key words: titanium tetrachloride; esterification; *n*-octylacetate; kinetic study; polymer supported catalyst

INTRODUCTION

Heterogenation of homogeneous catalysts by attaching them to polymers leads to improved stability and selectivity because the catalysts that are produced combine the advantages of the polymer and the homogeneous catalysts. The most important advantage in using a polymer supported catalyst in an organic reaction is the simplification of the reaction work-up; the need for complex chromatographic techniques can be avoided for product separation and isolation.^{1–12} Also, such a catalyst can often be reused many times without the loss of activity because the polymeric by-pro-

duct has the same structure as the polymer supported catalyst.

A thorough literature survey reveals the utility of titanium tetrachloride (TiCl_4) as a convenient synthetic route to various industrially and pharmaceutically important compounds.¹³ Even though TiCl_4 has many advantages in a homogeneous environment, it has drawbacks such as its corrosive nature, moisture sensitivity, less stability at room temperature, handling difficulty, and a hazardous nature. Attempts have been made to synthesize TiCl_4 anchored onto an insoluble polymer matrix in order to overcome the disadvantages of soluble TiCl_4 .^{13,14}

Studies reported in the literature reveal that the utility of a poly(4-vinylpyridine-*N*-oxide)-titanium tetrachloride (PVPNO- TiCl_4) complex in organic reactions has not been studied. This article describes the preparation of crosslinked copoly-

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mer beads of the PVPNO-TiCl₄ complex. This complex shows good catalytic activity in organic reactions such as esterification and acetal and ketal formation. Herein we report on the preparation of the catalyst and the kinetics and mechanism of formation of *n*-octylacetate from acetic acid and *n*-octanol.

EXPERIMENTAL

Materials

Styrene (Fluka), divinylbenzene (DVB, Polyscience, ICPA), polyvinyl alcohol (Fluka), gelatin (AR, BDH), *n*-octanol, and titanium tetrachloride (Johnson Matthey Alfa Products) were used as received. 4-Vinyl pyridine (Fluka) was distilled under reduced pressure. AIBN (Kochlight) was recrystallized from ethanol. The reaction mixtures were stirred by a mechanical stirrer (Tullu FHP motor, UP National Mfrs. P. Ltd.), and the stirring speed was measured using a tachometer (Teclock). GC analyses were performed on a Varian 3700 with a Vista CDS 401 data system having a flame ionization detector with a 2 m × $\frac{1}{8}$ in. column of 10% carbowax on 80–100 chrom WHP.

Synthesis of PNO-TiCl₄ Complex

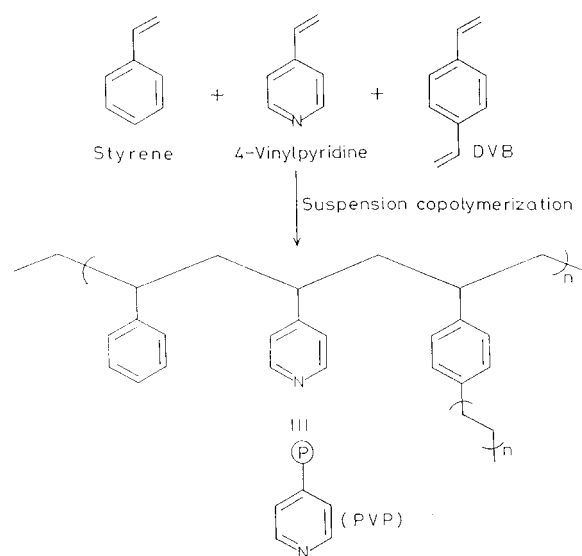
The PNO (0.2 mol) was dissolved in 150 mL of chloroform, and 0.2 mol titanium tetrachloride was added to the homogeneous solution. The mixture was stirred for 1 h at room temperature. The PNO-TiCl₄ complex was filtered under a vacuum and repeatedly washed with chloroform (3 × 150 mL). The complex (hygroscopic, containing 48.9% of chloride ion) was stored in a vacuum desiccator.

Synthesis of PVP Beads

The method described for the preparation of crosslinked copolymers of vinyltoluene¹⁵ by the suspension copolymerization technique was adopted as such for the preparation of copolymers of styrene and VP crosslinked with DVB (Scheme 1). Polymers with different percentages of crosslinking (2–10%) by weight of DVB and different percentages of active sites (25, 50, and 75%) by weight of VP were also prepared.

Synthesis of PVPNO and Its TiCl₄ Complex

The crosslinked copolymer of PVPNO was prepared¹⁶ by adding 35% hydrogen peroxide (50

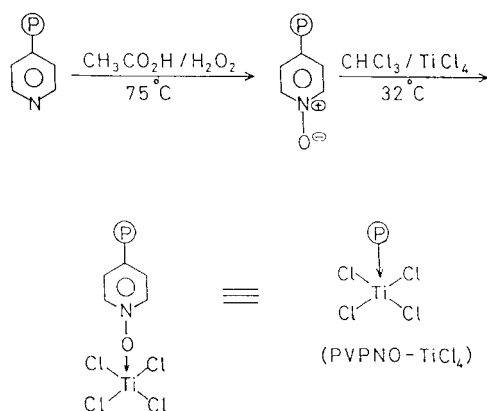


Scheme 1 The preparation of crosslinked copolymers of vinylpyridine.

mL) to the corresponding PVP (25 g) in glacial acetic acid (300 mL) while maintaining the temperature at 75°C for 12 h. Further portions (15 mL) of hydrogen peroxide were added after 3 and 6 h. Acetic acid was removed by filtration. The resulting solid was suspended in 150 mL of double distilled water and then basified with an excess of sodium hydroxide solution (10% w/w). Then the polymer beads were thoroughly washed with an excess of water, ethanol, and acetone. The resulting polymer beads (PVPNO) were dried in a vacuum at 50°C for 12 h.

The insoluble PVPNO beads (20 g) were converted into the titanium tetrachloride complex by swelling them in chloroform (150 mL) and stirring with titanium tetrachloride (15 mL) for 9 h at room temperature (32°C) and then cooling (0–10°C). The beads were filtered, washed with chloroform and acetone, and dried under a vacuum at 50°C for 24 h. The steps involved in the preparation of the PVPNO-TiCl₄ complex are given in Scheme 2.

The polymer supported PVPNO-TiCl₄ beads were sieved into different particle sizes (–60 + 80, –80 + 120, –120 + 170, and –170 + 200 mesh, U.S. standard). The chloride ion concentrations were estimated according to the oxygen flask method^{17,18} and were found to be 3.21, 6.43, and 9.64 meq of chloride/1 g of PVPNO-TiCl₄ for 25, 50, and 75% active sites (with respect to the pyridine group of the polymer) on the polymer, respectively.



Scheme 2 The synthesis of the PVPNO-TiCl₄ complex.

IR Spectral Analysis of PVPNO-TiCl₄

The IR (Perkin Elmer 598 Spectrophotometer) spectrum of PVPNO showed an absorption band at 1230 cm⁻¹ that represents the N—O stretching frequency (consistent with the reported value¹⁹). The PVPNO-TiCl₄ complex showed an absorption maximum at about 1205 cm⁻¹, indicating a reduction in the electron density on the oxygen that was due to the 1 : 1 (polymeric ligand to titanium tetrachloride) complex. A similar band at 1205 cm⁻¹ was observed for the PNO-TiCl₄ complex, which confirmed the O—Ti stretching for the PVPNO-TiCl₄ complex.

Typical Kinetic Experiment

n-Octanol (3.0 mL, 19.05 mmol) and acetic acid (25.0 mL, 437 mmol) were added to a 150-mL three-necked round-bottomed flask fitted with a double walled condenser, which was placed in a thermostat maintained at 50 ± 0.2°C and stirred mechanically with a 45 × 18 mm curved Teflon blade at 400 rpm for 10 min to condition the substrate. The PVPNO-TiCl₄ complex (0.8 g, 2% crosslinked, -60 + 80 mesh, 50% active site) was added to the reaction mixture after a sample was drawn at zero time. Then samples were collected at regular intervals and analyzed using GC. The amount of *n*-octanol that disappeared from the reaction mixture was estimated, and the pseudo first-order rate constants were calculated from plots of the log(*a* - *x*) versus time, where (*a* - *x*) is the concentration of *n*-octanol at a given time *t*. The results are discussed in the following sections.

Effect of Stirring Speed

Table I shows the effect of stirring speed (0–800 rpm) on the rate constant for the esterification of

Table I Effect of Stirring Speed

Stirring Speed (rpm)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
0	0.73
200	1.13
400	2.49
600	3.33
800	3.45

The effect was on the rate constant for the reaction with a 2% crosslinked, -60 + 80 mesh, 50% active site catalyst at 50°C.

n-octanol with acetic acid by 2% crosslinked, -60 + 80 mesh, 50% active site (with respect to the amount of VP) PVPNO-TiCl₄. It was found to be dependent on the stirring speed. This indicates that stirring the mixture mechanically caused an increase in the rate constant, which was due to the promotion of contact between the catalyst and substrates, thereby enabling more substrate to react. The reaction was under mass transfer control.¹⁵

Effect of Catalyst Amount and Substrate Concentration

The observed rate constant linearly increased with the 400–1600 mg of the 2% crosslinked, -60 + 80 mesh, 50% active site catalyst used (0.4–1.6 g) at a fixed concentration of *n*-octanol (3.0 mL, 19.05 mmol) and acetic acid (25.0 mL, 437 mmol). The pseudo first-order rate constant was directly proportional to the catalyst loading because the surface area and the total number of active sites increased linearly with it (Table II). The increased rate constant with an added catalyst amount indicates that the rate-limiting step of

Table II Effect of Catalyst Amount

Catalyst Amount		$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
g	meq	
0.4	2.57	1.35
0.8	5.14	2.49
1.2	7.71	3.55
1.6	10.28	4.89
2.0	12.85	6.30

The effect was on the rate constant for the reaction with 2% crosslinked, 50% active site, -60 + 80 mesh size catalyst at 400 rpm and 50°C.

Table III Effect of *n*-Octanol Concentration

<i>n</i> -Octanol		$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
mL	mmol	
1.5	9.53	2.10
3.0	19.00	2.49
4.5	28.58	2.92
6.0	38.10	3.41
9.0	57.15	3.62

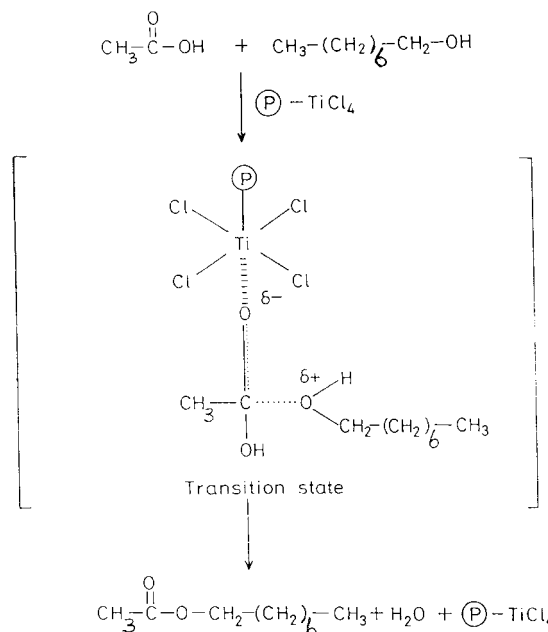
The effect was on the rate constant for the reaction with 2% crosslinked, 50% active site, -60 + 80 mesh size catalyst at 400 rpm and 50°C.

the reaction takes place within or on the surface of the catalyst.^{7,13}

The effect of substrate concentration on the rate of the reaction was investigated by varying the amount of *n*-octanol from 1.5 mL (9.53 mmol) to 9.0 mL (57.15 mmol). The observed rate constant for the formation of *n*-octylacetate increased on increasing the concentration of *n*-octanol but keeping the other experimental conditions fixed. The experimental results are shown in Table III. A similar observation was reported earlier by Yadav and Mehta²⁰ for the esterification of acetic acid with cyclohexanol and phenethyl (2-phenylethanol) using solid acidic catalysts such as Filtrol-24, amberlyst-15, sulfated zirconia, and heteropolyacids (supported on silica and carbon). We believe that during the reaction the polymer supported titanium tetrachloride, acetic acid, and *n*-octanol form a ternary complex in the transition state, which on decomposition gives the product. Under the experimental conditions, no other product was observed. Therefore, the Lewis site of the titanium center complexes with only the carboxylic acid and not with alcohol (Scheme 3). Blossey et al. also reported the same type of transition state for the esterification of *n*-butanol with acetic acid, propionic acid, and benzoic acid using polystyrene bound aluminum chloride as the catalyst.²¹

Effect of Particle Size

In this study four ranges of different particle (mesh) sizes with the same characteristics of the PVPNO-TiCl₄ catalyst were employed to investigate the effect of particle size on the formation of *n*-octylacetate. The results (Table IV) indicate that a high conversion is obtained for using a small mesh size catalyst pellet. Smaller particles

**Scheme 3** The mechanism for the formation of *n*-octylacetate.

provide larger exposure of the surface area and provide a smaller reaction path, so the utilization of the active site of the catalyst by the reactants is higher. Hence, the reaction rate increased on decreasing the size of the particles.

Effect of Crosslinking

The reaction rate was found to be highly dependent on the degree of crosslinking. The functional group capacity (TiCl₄) was found to be maximum with 2% crosslinked resin. It gradually decreased as the degree of crosslinking was increased to 4, 6, 8, and 10%. The variation of the rate constants as a function of the degree of crosslinking is represented in Table V. A low value of the equivalent activity of the catalyst was obtained when using a higher degree of crosslinked polymer. This may be

Table IV Effect of Particle Size

Particle Size (Mesh)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
-60 + 80	2.49
-80 + 120	3.56
-120 + 170	4.05
-170 + 200	4.51

The effect was on the rate constant for the reaction with 2% divinylbenzene and a 50% active site at 400 rpm and 50°C.

Table V Effect of Crosslinking

DVB (%)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
2	2.49
4	2.15
6	2.05
8	1.72
10	1.43

The effect of the variation of the percent crosslinking with divinylbenzene (DVB) was on the rate constant for the reaction with a 50% active site, -60 + 80 mesh size catalyst at 400 rpm and 50°C.

because the degree of crosslinking controls the diffusion rates by controlling the swelling of the polymer matrix.^{13,22,23}

Effect of Percentage of Active Sites

Table VI shows the rate of ester formation with an increased percentage of active sites (ring substitution) of the PVPNO-TiCl₄. The catalytic activity of the reaction increased with an increase of VP from 25 to 75% in the original polymer. The higher activity in the more functionalized polymers may be attributed to the increased swelling of the catalyst. Therefore, the intraparticle diffusion and intrinsic reactivity also increases. Hence, the rate constant increases on increasing the percent active site of the catalyst.^{13,24,25}

Control Experiments

Control experiments were carried out with 0.8 g of 2% crosslinked, 50% active site, -60 + 80 mesh unfunctionalized PVPNO and a no catalyst condition; less than 5% esterification occurred in 1 h for the above two cases.

The esterification reactions were also carried out under homogenous conditions with 6.43 meq of TiCl₄ on the PNO-TiCl₄ complex. The reaction rate constants were found to be ≈ 3.5 and 2 times faster, respectively, as compared with the polymer supported titanium tetrachloride (PVPNO-TiCl₄).

Reuse of Catalyst

After completion of the esterification reaction the polymer supported titanium tetrachloride could be easily recovered from the reaction mixture by ordinary filtration, and it was reused 4 times without any discernable change of activity.

Effect of Temperature

The rate constant of the esterification reaction was measured at different temperatures (40–60°C) and was found to be temperature dependent. The rate of the reaction increased with an increase in the temperature, and the energy of activation was determined ($E_a = 58.8 \text{ kJ/mol}$) from an Arrhenius plot. The other thermodynamic parameters for the reaction were also determined: entropy of activation ($\Delta S^\ddagger = -141.7 \text{ eu}$), enthalpy of activation ($\Delta H^\ddagger = 55.8 \text{ kJ/mol}$), and free energy of activation ($\Delta G^\ddagger = 101.6 \text{ kJ/mol}$).

Reaction Mechanism

The esterification reaction catalyzed by cross-linked PVPNO anchored titanium tetrachloride is limited by the following factors:

1. mass transfer of the reactants from the bulk solution to the exterior surface of the catalyst particle;
2. diffusion of the reactants from the surface of the catalyst to the active catalytic site;
3. the chemical reaction itself;
4. diffusion of the products away from the active site to the catalyst particle surface; and
5. mass transfer of the products from the surface into the bulk solution.

The rate-limiting step of the esterification reaction may take place within or on the surface of the polymer because the rate of formation of the product increases linearly with the amount of the added catalyst. A higher negative entropy value indicates that the catalyst, acetic acid, and *n*-octanol probably form a more ordered transition state in the rate-limiting step. No other product was detected in the GC. Therefore, we infer there was no bond broken between carbon and oxygen in *n*-octanol.²¹ From the observed experimental

Table VI Effect of Percent Active Site

Active Site (%)	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$
25	1.62
50	2.49
75	4.11

The effect was on the rate constant for the reaction with a 2% crosslinked, -60 + 80 mesh size catalyst at 400 rpm and 50°C.

results we propose the mechanism shown in Scheme 3.

CONCLUSIONS

The synthesis of *n*-octylacetate (which is the only reaction product) by this method is clean with the absence of any other products such as *n*-octene. This method may be adopted for the industrial manufacture of *n*-octylacetate. The reaction obeys pseudo first-order kinetics. The effects of the operating conditions, such as reactant concentration, stirring speed, catalyst amount, degree of crosslinking, percent of ring substitution of the polymer, and temperature, on the conversion were investigated in detail. The advantage of the polymer supported titanium tetrachloride complex is that it is insoluble, easily recoverable from the reaction mixture by filtration, and reusable. Hence, it can be considered as a potential catalyst for esterification reactions.

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