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Synthesis and properties of β-diketonato metal complexes as a catalyst for the synthesis of polyurethane

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ABSTRACT

The catalytic activity of ethyl acetoacetato complexes on the synthesis of urethane was investigated to develop a novel catalyst in the place of dibutyltin dilaurate. Ethyl acetoacetato complexes were prepared by the reaction of ethyl acetoacetate with aluminum chloride, copper acetate, ferric chloride, zinc oxide, or zirconium tetrachloride. The catalytic activity was determined for the reaction of poly(propylene glycol) (molecular weight: 400) with hexamethylene diisocyanate at room temperature. The aluminum, zinc, and zirconium chelates provided colorless and transparent polyurethanes. The iron and copper chelates gave polyurethanes colored in red and blue, respectively. Tetra(ethyl acetoacetato)zirconium showed high reactivity compared with that of tetrakis(acetylacetonato)zirconium. The higher reactivity of ethyl acetoacetato chelates compared to those of acetylacetonato chelates would be due to the weaker coordination of ethyl acetoacetato group to show the higher solubility in organic solvents and lower crystallinity of ethyl acetoacetato chelates. The reactivity was also determined by the rate constant at the early stage of the polymerization. The rate constants were arranged in the following order: $Zr(etac)_4$ > $Zn(etac)_2$ > $SnBu_2(OLauryl)_2$ > $Al(etac)_3$. The ethyl acetoacetato chelates of zinc and zirconium were found to have higher catalytic activity compared to that of dibutyltin dilaurate.

1. INTRODUCTION

Polyurethanes are widely used in our daily life because of their good properties such as anti-abrasion and heat-resistivity. Tin compounds are generally used as a polyurethane synthesis catalyst which is reported the toxicity (Horiguchi 1995) and limitation of usage (Commission Regulation (EU) 1995). Therefore, new catalysts are widely and energetically to substitute the tin catalysts. Zirconium acetylacetonate ($Zr(acac)_4$) is a powerful candidate in this field because of its high catalytic activity and lower coloration of the polymer (Blank 1999). The demerits of this compound is,

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however, the low solubility in organic solvents to produce a translucent polymer due to the insoluble catalyst in polyurethane.

Metal complexes having ethyl acetoacetonate (Hetac) as ligand are expected to be substituted catalysts in the polyurethane synthesis because these complexes show some characteristic properties such as a low chelating ability to metal due to the asymmetrical structure, increasing intramolecular polarization due to the ethoxy group, and lower chelating ability compared with acetylacetone.

In this work, ethyl acetoacetato metal complexes were investigated as a novel catalyst in the polyurethane synthesis to substitute tin compounds.

2. PREPARATION OF METAL CHELATES

Tris(acetylacetonato)aluminum ($Al(acac)_3$) was synthesized by the reaction of aluminum trichloride with acetylacetone in the presence of triethylamine and isolated by recrystallization as a pale-yellow crystal in 88 % yield.

Tris(ethyl acetoacetato)aluminum ($Al(etac)_3$) was synthesized by the reaction of aluminum trichloride with ethyl acetoacetate in the presence of triethylamine and isolated by recrystallization as a white crystal in 85 % yield.

Bis(acetylacetonato)copper ($Cu(acac)_2$) was synthesized by the reaction of copper diacetate with acetylacetone and isolated by recrystallization as a blue crystal in 84 % yield.

Bis(ethyl acetoacetato)copper ($Cu(etac)_2$) was synthesized by the reaction of copper diacetate with ethyl acetoacetate and isolated by recrystallization as a green crystal in 73 % yield.

Tris(acetylacetonato)iron ($Fe(acac)_3$) was synthesized by the reaction of iron trichloride with acetylacetone in the presence of triethylamine and isolated by recrystallization as a red crystal in 94 % yield.

Tris(ethyl acetoacetato)iron ($Fe(etac)_3$) was synthesized by the reaction of iron trichloride with ethyl acetoacetate in the presence of triethylamine and isolated by recrystallization as a red crystal in 64 % yield.

Bis(acetylacetonato)zinc ($Zn(acac)_2$) was synthesized by the reaction of zinc oxide with acetylacetone and isolated by recrystallization as a white crystal in 88 % yield.

Bis(ethyl acetoacetato)zinc ($Zn(etac)_2$) was synthesized by the reaction of zinc dichloride with ethyl acetoacetato sodium and isolated by sublimation as a white powder in 32 % yield.

Tetrakis(acetylacetonato)zirconium ($Zr(acac)_4$) was synthesized by the reaction of zirconium tetrachloride with acetylacetone in the presence of triethylamine and isolated by recrystallization as a pale-yellow crystal in 70 % yield.

Tetrakis(ethyl acetoacetato)zirconium ($Zr(etac)_4$) was synthesized by the reaction of zirconium tetrachloride with ethyl acetoacetate in the presence of triethylamine and isolated by recrystallization as a white crystal in 68 % yield.

3. DETERMINATION OF CATALYTIC ACTIVITY OF METAL CHELATES

The catalytic ability of metal complex was determined by the following procedure: metal complex was dissolved in poly(propylene glycol) (PPG, weight average molecular

weight 400) in a 100-mL vial. Hexamethylene diisocyanate (HDI) was added to this solution in the molar ratio of PPG:HDI:catalyst=1.05:1.0:0.001 and then stirred at room temperature. After 0.5, 1, 2, 4, and 8 min, polymerization was terminated by addition of dibutylamine which reacts with residual isocyanato group. The amount of residual dibutylamine was determined by titration using 0.5-mol/L hydrochloric acid. The conversion of isocyanato group was calculated by the equation (1):

$$\text{conversion of isocyanato group (\%)} = 0.5 \times f \times (V_0 - V) / 1000 / (2 \times X_{HDI} / M_{HDI}) \quad (1)$$

0.5: concentration of hydrochloric acid (mol/L);
f: factor of hydrochloric acid;
V_0: volume of hydrochloric acid used in the blank test (mL);
V: volume of hydrochloric acid used in the titration of the sample (mL);
X_{HDI}: weight of HDI used in the test (g);
M_{HDI}: molecular weight of HDI (168.20 g/mol).

The reaction constant was calculated by the equation (2) (Li 2000):

$$1 / (1 - r / 100) = k_2 \times t + C \quad (2)$$

r: conversion of isocyanato group (%);
k_2: second-order rate constant (mol^{-1} min^{-1});
t: time (min);
C: constant.

By using the metal complexes shown in the above paragraph, polymerization took place and polyurethane was formed. Relatively transparent polyurethanes were obtained except for the copper and iron catalysts which gave red and blue polymers, respectively. In every metal, the etac complex showed high activity compared with the acac complex. The high solubility in organic solvents and low crystallinity may affect the rate of polymerization.

The rate constants of etac complexes were calculated as follows: 3.00×10^{-3} mol^{-1} min^{-1} ($Al(etac)_3$), 7.23×10^{-2} $mol^{-1}min^{-1}$ ($Zn(etac)_2$), 1.37 $mol^{-1}min^{-1}$ ($Zr(etac)_4$), and 2.61×10^{-2} $mol^{-1}min^{-1}$ ($SnBu_2(OLauryl)_2$, DBTDL). $Al(etac)_3$ showed the minimum value among these etac complexes because of the lower atomic radius to be difficult in the attack of hydroxyl group in PPG. $Zn(etac)_2$ showed high activity compared with DBTDL at the initial stage of polymerization but the conversion was decreased over 50 %. The conversion of one isocyanato group in HDI would make it difficult to form a complex with the second isocyanato group in this catalyst. On the other hand, $Zr(etac)_4$ showed an excellent activity compared with DBTDL. The empty orbital on zirconium atom may help the formation of intermediate with isocyanato group in HDI.

As a result, ethyl acetoacetato complexes were found to be good catalyst for polyurethane synthesis compared with acetylacetonato complexes. The activity was increased in the order of $Al(etac)_3 < SnBu_2(OLauryl)_2 < Zn(etac)_2 < Zr(etac)_4$. $Zr(etac)_4$ was found to be a good catalyst to substitute tin catalyst in the polyurethane synthesis.

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