

NOTES

Amine-Manganese Complex as an Efficient Catalyst for Polyurethane Syntheses

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The polyurethane industry has progressed rapidly, and reactions of polyols and isocyanates are well-known technological processes. The chemical structure of polyurethane is diverse, and as physical properties are discovered, the wide use of polyurethane is spreading accordingly. But there exists a problem: discoloration by air and light. In general, aliphatic isocyanate is used to resolve this problem. However, the reaction rate of aliphatic isocyanates on preparations of polyurethane is very slow compared with aromatic isocyanates. Therefore, tertiary amines¹⁻⁵ and tin compounds,⁶⁻¹⁰ having excellent catalytic activity, are used mainly as catalysts for polyurethane formation. In particular, dibutyltin dilaurate (DBTDL) has been used. However, tin is toxic to human beings. Accordingly, a new catalyst or catalytic system is necessary to replace this catalyst. Recently, late transition metal complexes such as metal- β -diketone complexes ($Mt(acac)_n$) are being researched with great interest.¹¹⁻¹³ For example, $Fe(acac)_3$ and $Cu(acac)_2$ complexes are used for the reaction between hexamethylene diisocyanate (HDI) and alcohols.^{14, 15} Although there is sufficiently the catalytic activity for only $Mt(acac)_n$ complexes, the increase of the catalytic activity is expected by the co-catalyst. The co-catalyst plays important roles in many reactions. On urethane formation reaction, triphenyl bismuth (TPB)-hexafluoroacetylacetonato (f_6acac) catalytic system shows high catalytic activity and the existence of the co-catalyst such as f_6acac is important to the reaction.¹⁶

In the present paper, the activities of $Mt(acac)_n$ and tertiary amine- $Mt(acac)_n$ catalyst as new group catalytic system are described. The data clearly show that instead of DBTDL, the tertiary amine- $Mt(acac)_n$ can be used for catalyst of the reaction between HDI and alcohol.

EXPERIMENTAL

Materials

HDI and diethylene glycol (DEG) (Nacalai Tesque Inc.) were used immediately after distillation under reduced pressure. Manganese(II) ($Mn(acac)_2$), and iron(III) acetylacetonates ($Fe(acac)_3$) (Nacalai Tesque Inc.), cobalt (II) ($Co(acac)_2$), nickel (II) ($Ni(acac)_2$), copper (II) acetylacetonates ($Cu(acac)_2$), and dibutyltin dilaurate (DBTDL) (Tokyo Kasei Kogyo Co., Ltd.) were used as received. Triethylenediamine (TEDA), N,N,N',N'',N'' -pentamethyldiethylenetriamine (DT), N,N,N',N' -tetramethylethylenediamine (TE), bis(2-dimethylaminoethyl) ether (ETS), N,N',N' -trimethylaminoethylpiperazine (NP) were delivered by Tosoh Co., Ltd. Toluene and N,N -dimethylformamide (DMF) (Nacalai Tesque Inc.) were dehydrated over a molecular sieve (4 Å) at room temperature for about 24 h before use. Di-*n*-butylamine and bromo cresol green (Nacalai Tesque Inc.) were used as received.

Reaction between HDI and DEG Catalyzed by Metal- β -Diketone

The reaction was performed under an argon atmosphere in a 200 mL three-necked glass vessel. In a typical experiment, 0.0897 g (0.31 mmol) of $Mn(acac)_2$, 0.0348 g (0.31 mmol) of TEDA, 1.040 g (6.20 mmol) of HDI and 15 mL of DMF were placed in a 20 mL Schlenk tube. A 0.660 g (6.20 mmol) of DEG and 65 mL of DMF were placed in a 200 mL three-necked glass vessel.

The TEDA-metal complex with HDI in DMF solution and DEG-DMF solution were stirred at the desired reaction temperature (for example: 30°C) for 30 min., and the catalyst and HDI in DMF solution

Table II. Polyaddition reaction catalyzed by the TEDA-Mt(acac)_n complex between HDI and DEG^a

Catalyst	$k/L \text{ mol}^{-1} \text{ h}^{-1}$	$K_C \times 10^4/L^2 \text{ eq}^{-1} \text{ mol}^{-1} \text{ h}^{-1}$
none	0.2	—
TEDA-Mn(acac) ₂	102.2	2.8
TEDA-Fe(acac) ₃	49.3	1.3
TEDA-Co(acac) ₂	14.4	0.4
TEDA-Ni(acac) ₂	1.6	—
TEDA-Cu(acac) ₂	3.5	—

^a[Mt(acac)_n] = 0.0036 mol L⁻¹, [HDI] = [DEG] = 0.073 mol L⁻¹, Temp. = 30°C, Solvent = DMF, TEDA/Mt = 1 in mol ratio.

Table I. Polyaddition reaction catalyzed by the Mt(acac)_n complex without amines between HDI and DEG^a

Catalyst	$k/L \text{ mol}^{-1} \text{ h}^{-1}$	$K_C \times 10^4/L^2 \text{ eq}^{-1} \text{ mol}^{-1} \text{ h}^{-1}$
none	0.2	—
DBTDL	139.6	3.8
Mn(acac) ₂	52.3	1.4
Fe(acac) ₃	24.4	0.7
Co(acac) ₂	5.8	0.2
Ni(acac) ₂	1.7	—
Cu(acac) ₂	1.9	—

^a[Catalyst] = 0.0036 mol L⁻¹, [HDI] = [DEG] = 0.073 mol L⁻¹, Temp. = 30°, solvent = DMF.

were added to the DEG-DMF solution. After the reaction started, aliquots (8 mL) were removed from the reaction solution at regular time intervals (5 or 10 min) and predetermined excess di-*n*-dibutylamine solution (typically 10 mL of 1.0 mol L⁻¹) was added. Unreacted amine was back-titrated using standard hydrochloric acid (typically 0.5 mol L⁻¹) to a bromo cresol green end-point. The rate constant was calculated from simple second-order kinetics.

Characterization

Molecular weight and molecular weight distribution were determined by GPC using a Tosoh GPC-8020 in tetrahydrofuran (THF) at 40°C calibrated as standard polystyrenes. IR spectra (in KBr pellets) were recorded on a JASCO FT/IR-5300 spectrometer.

RESULTS AND DISCUSSION

Table I shows the reactions catalyzed by Mt(acac)_n between HDI and DEG at 30°C in DMF. From the theory of Farkas³ and Hostettler,⁴ the catalytic constant (K_C) was calculated as eq 1,

$$k = k_0 + K_C[\text{catalyst}]^n \quad (1)$$

and rate constants (k_0 : uncatalyzed system and k : catalyzed system) were calculated from simple second-order kinetics. The reaction between HDI and DEG did not proceed without a catalyst, but when the Mt(acac)_n complex was used as catalyst, the reaction between HDI and DEG proceeded speedily. The

Mn(acac)₂ catalyst reached a high conversion (> 80%) after 60 min and attained total conversion after 120 min, whereas Fe(acac)₃ showed 85% conversion after 120 min. Fe(acac)₃ catalyst has good to excellent catalytic activity for the reaction between HDI and ethanol.^{14,15} However, under our experimental conditions, the catalytic activity of Mn(acac)₂ was even higher, and the catalytic activity of Mn(acac)₂ was about twice that of Fe(acac)₃. Although the catalytic activity of Mn(acac)₂ was very high, it was lower (about 1/3) than the activity of DBTDL. The catalytic activity of Mt(acac)_n was lower than that of DBTDL because HDI was inert coordinated to Mt(acac)_n. Using metal together with amine, further catalytic activity is expected. Thus, we examined the effects of added amine toward polyaddition reaction catalyzed by Mt(acac)_n complexes.

Table II summarizes the effects of added TEDA to Mt(acac)_n complex. Although the reaction catalyzed by Mt(acac)_n proceeded, the reaction catalyzed by TEDA did not proceed and the co-catalyst such as TEDA was inactive. The order of catalytic activity was TEDA-Mn(acac)₂ > TEDA-Fe(acac)₃ > TEDA-Co(acac)₂ > TEDA-Ni(acac)₂ > TEDA-Cu(acac)₂, the same as in the case of reaction without TEDA. When TEDA-Mn(acac)₂ complex was used as catalyst, catalytic activity was two times more active than Mn(acac)₂. The catalytic activity of Mn(acac)₂ is improved, when TEDA is used as co-catalyst. The GPC elution curve of polyurethane obtained with TEDA-Mn(acac)₂ complex showed a mulch modal, and number average molecular weight (M_n) of the resulting polyurethane was 2700 (polyurethane conversion was 95%). This GPC elution curve was the same as that of DBTDL. The activity of this catalytic system using TEDA and Mn(acac)₂ was comparable to that of DBTDL, and this catalytic system will be replacing DBTDL catalytic system.

At the next step of the investigation, the effects of other amines such as DT, TE, ETS, and NP were examined. Table III summarizes the effects of added these amines to Mn(acac)₂ complex. These amines were inactive on the reaction. Mn(acac)₂ activated with TEDA showed fairly good catalytic activity (conversion was

Table III. Polyaddition reaction catalyzed by the amine-Mn(acac)₂ complex between HDI and DEG^a

Catalyst	$k/\text{L mol}^{-1} \text{h}^{-1}$	$K_C \times 10^4/\text{L}^2 \text{eq}^{-1} \text{mol}^{-1} \text{h}^{-1}$
none	0.2	—
TEDA-Mn(acac) ₂	102.2	2.8
DT-Mn(acac) ₂	40.6	1.1
TE-Mn(acac) ₂	39.9	1.1
ETS-Mn(acac) ₂	88.2	2.4
NP-Mn(acac) ₂	44.5	1.2

^a[Mn(acac)₂] = 0.0036 mol L⁻¹, [HDI] = [DEG] = 0.073 mol L⁻¹, Temp. = 30°C, Solvent = DMF, amine/Mn = 1 in mol ratio.

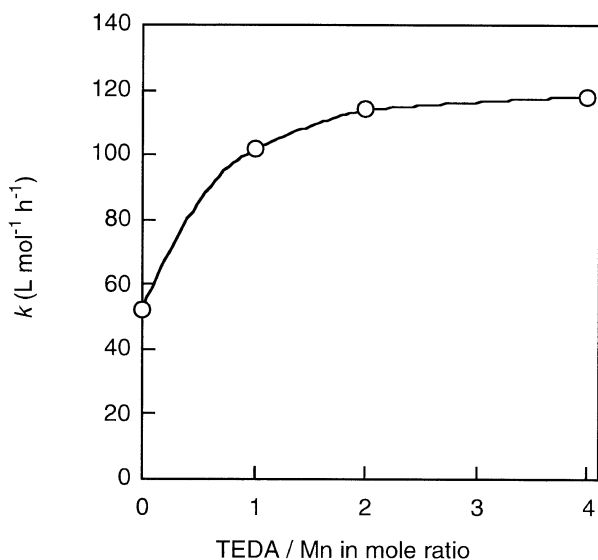


Figure 1. Effects of adding TEDA ([HDI] = [DEG] = 0.073 mol L⁻¹, [Mn(acac)₂] = 0.0036 mol L⁻¹).

95%), while other amines exhibited somewhat low catalytic activity (conversion was 75%).

The existence of a co-catalyst such as TEDA is important to this reaction. Thus, we examined the effects of the TEDA/Mn(acac)₂ molar ratio. Molar ratios of TEDA to Mn(acac)₂ changed from 1:1 to 2:1 and 4:1, as depicted in Figure 1. The activity of the catalyst was dependent on the TEDA/Mn(acac)₂ molar ratio. With increasing TEDA molar, the rate constant (k) increased. k , 102 when [TEDA]/[Mn(acac)₂] was 1, increased with this ratio, and was saturated around 120.

The reaction catalyzed by TEDA-Mn(acac)₂ between HDI and DEG was kinetically investigated. Figure 2 shows the time-reciprocal of isocyanate concentration plots in the temperature range 0–30°C. The reciprocal of isocyanate concentration linearly increased with reaction time. From an Arrhenius plot of k estimated from the plots in Figure 2, the overall activation energy (E_a) of the reaction between HDI and DEG was 58.4 kJ mol⁻¹. In the case of DBTDL, E_a was 71.4 kJ mol⁻¹. E_a of TEDA-Mn(acac)₂ complex is somewhat lower than that of DBTDL.

Figure 3 presents the relationship between k and catalyst concentration ([TEDA-Mn(acac)₂]). For wide

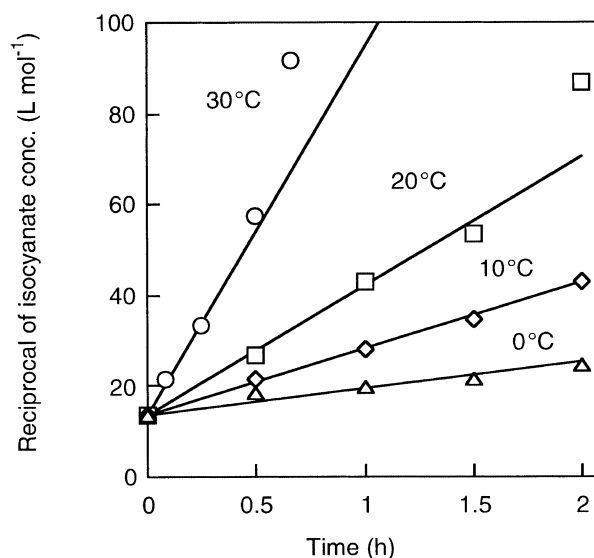


Figure 2. Time-reciprocal of isocyanate concentration plots in the reaction between HDI and DEG in DMF at different temperatures ([HDI] = [DEG] = 0.073 mol L⁻¹, [Mn(acac)₂] = 0.0036 mol L⁻¹, TEDA/Mn = 1 in mol ratio).

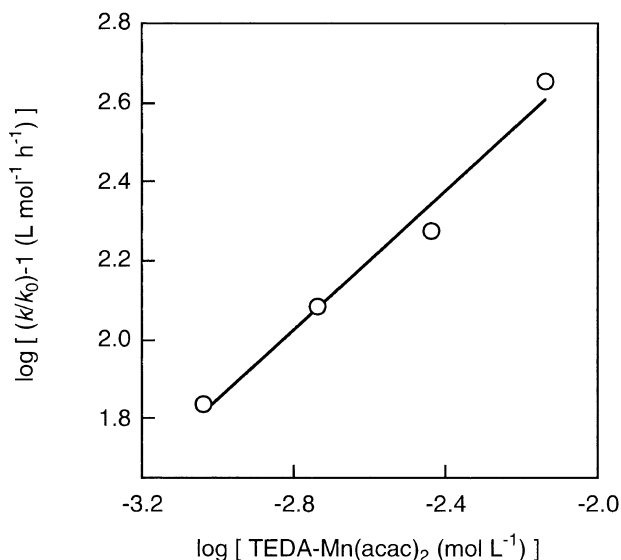


Figure 3. Dependence of k on TEDA/Mn(acac)₂ (1/1) catalyst concentration ([HDI] = [DEG] = 0.073 mol L⁻¹, TEDA/Mn = 1 in mol ratio, Temp. = 30°C, Solvent = DMF).

concentration range, the logarithmic expression was,

$$\log(k/k_0 - 1) = \log(K_C/k_0) + n \log[\text{TEDA-Mn(acac)}_2] \quad (2)$$

plots of $\log(k/k_0 - 1)$ vs. $\log[\text{TEDA-Mn}(\text{acac})_2]$ indicated a linear relation between k and $[\text{TEDA-Mn}(\text{acac})_2]$. k was proportional to 0.88 power of the $\text{TEDA-Mn}(\text{acac})_2$ concentration. From these results, the k is expressed as follows:

$$k = k_0 + K_c[\text{TEDA-Mn}(\text{acac})_2]^{0.88} \quad (3)$$

In the case of only $\text{Mn}(\text{acac})_2$, k was proportional to 1.00 power of the $\text{Mn}(\text{acac})_2$ concentration and this value was coincided with literature data.¹⁷ The 0.88 power observed here is lower than the 1.00 observed for the reaction catalyzed by $\text{Mn}(\text{acac})_2$. This suggests formation of a new complex by the HDI and TEDA coordination to $\text{Mn}(\text{acac})_2$.

To be clear structure of the resulting complex, FT-IR spectrum (in KBr pellet) of the complex was studied at $4600\text{--}400\text{ cm}^{-1}$. The coordination of HDI and $\text{Mn}(\text{acac})_2$ was achieved *via* oxygen or nitrogen atoms in the NCO group. The nitrile in the NCO group, coordinates to the metal with an accompanying upward shift of $20\text{--}50\text{ cm}^{-1}$ of CN stretching frequency.^{18,19} The FT-IR spectrum of $\text{HDI-Mn}(\text{acac})_2$ complex ($\text{HDI}:\text{Mn}(\text{acac})_2 = 1 : 1$) was found with appearance of the NCO peak at 2276 cm^{-1} . The nitrile in the NCO group was involved in coordination with an upward shift of 25 cm^{-1} in ν_{CN} , and the FT-IR spectrum showed coordination of HDI to $\text{Mn}(\text{acac})_2$ *via* nitrogen atom in the NCO group. FT-IR spectrum of mixture of TEDA, HDI, and $\text{Mn}(\text{acac})_2$ was found with appearance of the NCO peak at 2270 cm^{-1} . The relation between the NCO peak shift value and an affinity for complex was not clear, but TEDA will be coordinating HDI- $\text{Mn}(\text{acac})_2$ complex.

Kinetics and FT-IR did not clearly indicate a mechanism for the TEDA/HDI- $\text{Mn}(\text{acac})_2$ catalytic system for the polyaddition reaction between HDI and DEG. The mechanism will be clarified by further investigation.

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