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*NOTE*

# The Catalytic Characterization of Rare Earth Complexes Involving Silylene-Bridged Fluorenyl

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A group of rare earth complexes involving silylene-bridged fluorenyl have been synthesized; they can catalyze a series of methacrylate polymerization. From the results we can conclude that these kinds of complexes are highly active catalysts.

**Key Words: Rare earth, Complexes, Silylene-bridged fluorenyl, PMA, Catalysts.**

Polymethacrylates are important polymers in materials and surface-coating industries. Recently lanthanidocenes have been found to efficiently catalyze the living highly stereospecific polymerization of methyl methylacrylate. Yasuda *et al.*[1] and Marks *et al.*[2] have studied the activity of the $C_{2V}$ and $C_1$ symmetric lanthanidocenes for methyl methacrylate (MMA) polymerization. Yasuda *et al.*[1] first reported the polymer which has a high molecular weight, high melting point, low branching ratio and low polydispersity ($M_w/M_n$) using rare earth complexes such as $LnR(C_5R_5)_2$ and $Ln(C_5Me_5)_2$ as catalysts.

Recently, Qian *et al.*[3, 4] have reported the synthesis of Cs-symmetric lanthanidocenes and their catalytic behaviour to MMA polymerization. Rare earth complexes involving silylene-bridged fluorenyl that we synthesized are new complexes and have not been reported ever before. This work has studied the catalytic behaviur of polymerization of methyl methacrylate (MMA), ethyl methacrylate (EMA) and t-butyl methacrylate (BMA) and their applying fields are to be developed further.

Synthesis of the lanthanide complexes was carried out under purified argon using Schlenk techniques. THF and *n*-hexane were refluxed and distilled over the sodium ketyl of benzophenone under argon immediately before use. GPC was recorded on Water's 515/410/746, HR1, HR3, HR4 column; the velocity of flow is 1.0 mL/min.

The synthesis steps of rare earth complexes with silylene-bridged fluorenyl have been reported[5]. All polymerization reactions were carried out under argon. 10 mL of MMA (7.40 g, 74.0 mmol) was added to the solution of the initiator with vigorous magnetic stirring at the desired temperature. After a certain time, the polymerization was quenched with acidified methanol, and the polymer was

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precipitated. The resulting polymer was washed with methanol and dried in vacuum at 50°C.[6]

Similar method is used in PEMA, PBMA.

From Tables 1 and 2, we can conclude that rare earth complexes which we had synthesized have many characteristics as follows:

TABLE-1
POLYMERIZATION OF MMA

| Catalyst | Monomer | $10^3$ $M_n$ | $M_w/M_n$ | rr | rm | mm | Conv (%) | T(°C) | Time (h) |
|---|---|---|---|---|---|---|---|---|---|
| [$C_{33}H_{24}SiSmCl$] | MMA | 17 | 1.32 | 64.2 | 29.7 | 6.3 | 45 | 15 | 22 |
| [$C_{33}H_{24}SiSmCl$] | MMA | 47 | 1.22 | 62.2 | 31.3 | 5.9 | 10 | 60 | 22 |
| [$C_{33}H_{24}SiSmCl$] | MMA | 12 | 1.41 | 51.7 | 36.2 | 12.1 | 61 | 0 | 22 |
| [$C_{33}H_{24}SiSmCl$] | MMA | inactivity | — | — | — | — | — | –78 | 22 |
| [$C_{33}H_{24}SiSmCl$] | EMA | 126 | 1.25 | 60.9 | 32.3 | 6.8 | 54 | 60 | 22 |
| [$C_{33}H_{24}SiSmCl$] | BMA | — | — | — | — | — | — | 60 | 60 |

Conditions: Solvent: THF, cat/MA (mol/mol) = 1 : 500, MA/solvent (v/v) = 1 : 1.

TABLE-2
POLYMERIZATION OF MMA WITH DIFFERENT RARE EARTH METALLOCENES

| Catalyst | $10^3$ $M_n$ | $M_w/M_n$ | Conv. (%) | T (°C) | Time (h) |
|---|---|---|---|---|---|
| [$C_{33}H_{24}SiNdCl$] | 93 | 1.61 | 0.8 | 15 | 8 |
| [$C_{33}H_{24}SiDyCl$] | 434 | 1.42 | 0.6 | 15 | 8 |
| [$C_{33}H_{24}SiYbCl$] | 48 | 1.64 | 73 | 60 | 48 |
| [$C_{33}H_{24}SiLaCl$] | 156 | 1.52 | 79 | 60 | 48 |
| [$C_{33}H_{24}SiPrCl$] | 148 | 2.61 | 76 | 60 | 48 |

Conditions: Solvent: THF, cat./MMA (Mol/Mol) = 1 : 500, MMA/solvent (v/v) = 1 : 1.

The reaction temperature has great effects on the MMA polymerization (Table-1), the activities of $C_{33}H_{24}SiSmCl$ show higher activity in 0°C than in 15°C and 60°C; at higher reaction temperature, the molecular weight of (MMA) is low, and the molecular weight distribution is narrow. The molecular weight increases dramatically when the reaction temperature is lowered, but the molecular weight distribution becomes broad.

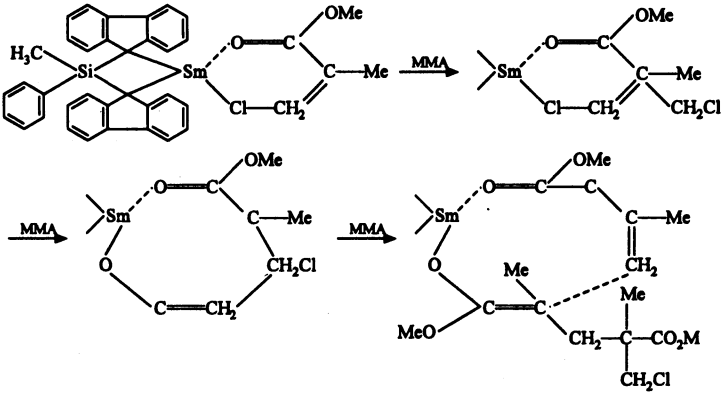
A group of rare earth complexes involving $C_{33}H_{24}SiSmCl$ can initiate moderately syndiospecific polymerization of MMA at 0–60°C; the mm content in Table-1 increases with reaction temperature decreasing[7, 8], but in PBMA at 60°C we did not get the polymer, may be because the reaction temperature is high or the reaction time is not too long.

The effects of solvent on the polymerization initiated by $C_{33}H_{24}SiSmCl$ were studied. It was found that only in THF, it shows high activity, but in toluene and ether it shows little activity, may be because the reaction time is too short.

$C_{33}H_{24}SiSmCl$ can also catalyze the ethyl methacrylate polymerization (PEMA). And we also get the high molecular weight and the narrow molecular distribution (Table-1).

Polymerization of MMA with different metal ions of $C_{33}H_{24}SiLnCl$ were also investigated (Table-2). At 60°C after 48 h reaction, the activites of $C_{33}H_{24}SiLnCl$ decrease in the following order: ($La^{3+}$) > ($Pr^{3+}$) > ($Yb^{3+}$); these orders are in agreement with the decreasing order of ionic radii, $La^{3+}$ (1.061 Å) > $Pr^{3+}$ (1.013 Å) > $Yb^{3+}$(0.858 Å), similar to that found in $(C_5Me_5)_2Me(THF)_2$[1b] (Table-2).

According to the coordinating polymerization mechanism proposed by Yasuda[1b], the **Scheme-1** is as follows:



**Scheme-1**

$C_{33}H_{24}SiSmCl$ as a catalyst reacts with MMA, forming allyl alcohol. Lanthanide complexes with octa ring, can initiate MMA polymerization, producing PMMA with high yield and narrow distribution. So we may conclude that the initiating reaction is that the complexes attack $CH_2$ group of MMA, forming $Ln—O—C(OCH_3)=C(CH_2)_2$; the second MMA molecule reacts with it in the same way as 1,4-Michael addition, producing intermediate with octa ring structure; the growth reaction is that the monomer attacks the growth end of octa ring and gives out the matching ester group.

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