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The Catalytic Behaviour of Rare Earth Complexes Containing Piperonal Dimethyl Acetal and Dicyclopentadienyl

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A number of rare earth complexes containing piperonal dimethyl acetal and dicyclopentadienyl 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, Piperonal dimethyl acetal, Dicyclopentadienyl, PMA, Catalysts.

INTRODUCTION

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 methacrylate (PMMA). Yasuda *et al.*[1] and Giardello *et al.*[2] have studied the activity of the C_{2V} and C_1 symmetric lanthanidocenes for methyl methacrylate 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. Organolanthanide hydrides $(Cp'_2LnH)_2$ and $(Me_2SiCp''_2LnH)_2$ ($Cp' = \eta^5$-Me_3C_3 and $Cp'' = \eta^5$-Me_4C_5) effectively and selectively catalyze a variety of olefin transformations including hydrogenation, oligomerization and polymerization.[3]

Recently, Qian *et al.*[4] have reported the synthesis of C_s-symmetric lanthanidocenes and their catalytic behaviour to methyl methacrylate polymerization. We have recently reported the rare earth complexes containing piperonal dimethylacetal and dicyclopentadienyl containing Ln—C bond.[5] This experiment studies the catalytic behaviour of polymerization of methyl methacrylate (MMA), ethyl methacrylate (EMA) and t-butyl methacrylate (BMA) and their applying fields are to be developed further.

EXPERIMENTAL

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 Waters 515/410/746, HR1, HR3, HR4 column; the velocity of flow is 1.0 mL/min.

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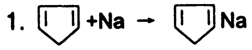
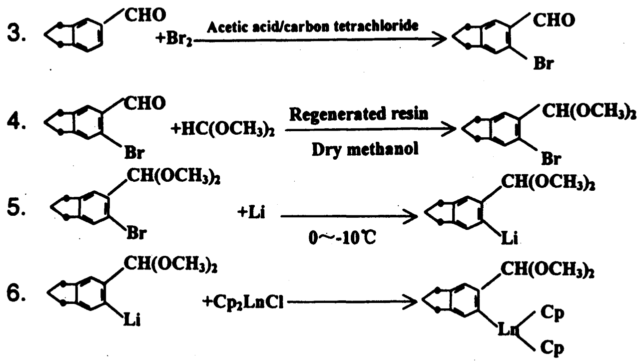
Scheme-1[8–11]



2. $LnCl_3+2CpNa \rightarrow Cp_2lnCl+2NaCl$

Complexes	1	2	3	4	5
Ln	Yb	Dy	Pr	La	Sm



The synthesis of these complexes has already been reported from this laboratory[5].

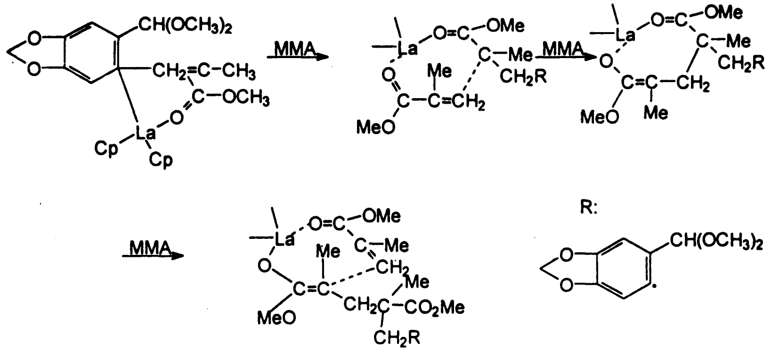
Polymerization of MMA, EMA, BMA.[12]

All polymerization reactions were carried out under the atmosphere of argon. Methyl methacrylate polymerization (PMMA) 10 mL (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 precipitated. The resulting polymer was washed with methanol and dried in vacuum at 50°C.

Similar method is used in ethyl methacrylate polymerization (PEMA) and *t*-butyl methacrylate polymerization (PBMA).

RESULTS AND DISCUSSION

Scheme-2



From the Tables 1 and 2, we conclude that these rare earth complexes have many characteristics as follows:

TABLE-1
POLYMERIZATION OF MMA, EMA AND BMA

Catalyst	Monomer	10^3 M_n	M_w/M_n	rr	rm	mm	Conv. (%)	T (°C)	Time (h)
[$C_{10}H_{11}O_4LaCp_2$]	MMA	72	1.61	62.7	24.6	12.7	65	15	22
[$C_{10}H_{11}O_4LaCp_2$]	MMA	47	1.22	61.3	25.6	13.1	10	60	22
[$C_{10}H_{11}O_4LaCp_2$]	MMA	89	1.81	63.9	25.2	10.9	72	0	22
[$C_{10}H_{11}O_4LaCp_2$]	MMA	inactivity	—	—	—	—	—	78	22
[$C_{10}H_{11}O_4LaCp_2$]	EMA	413	1.16	65.1	24.9	—	24	60	20
[$C_{10}H_{11}O_4LaCp_2$]	BMA	361	1.22	—	—	—	21	60	36

Conditions: cat/MMA (Mol/Mol) = 1 : 500, MMA/solvent (v/v) = 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)
[$C_{10}H_{11}O_4DyCp_2$]	101	1.46	10	15	22
[$C_{10}H_{11}O_4PrCp_2$]	272	1.47	18	15	22
[$C_{10}H_{11}O_4SmCp_2$]	236	1.19	15	15	22
[$C_{10}H_{11}O_4DyCp_2$]	281	1.19	8	60	50
[$C_{10}H_{11}O_4SmCp_2$]	215	1.40	10	60	50
[$C_{10}H_{11}O_4PrCp_2$]	148	2.61	20	60	50

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

The reaction temperature has great effects on the MMA polymerization (Table-1). The activities of $C_{10}H_{11}O_4LaCp_2$ 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 weights increased dramatically when the reaction temperature was lowered; the molecular weight distribution becomes broad.

$C_{10}H_{11}O_4LaCp_2$ can initiate moderately syndiospecific polymerization of MMA at 0–60°C; the mm content increased with reaction temperature increasing[6, 7], but in PEMA, we did not get the mm content, because the CH_3 group in ethyl may cover the mm peak in α-CH_3 group, and also in PBMA, we could not get the rr, mr, mm content, because of the same reason.

The effects of solvent on the polymerization initiated by $C_{10}H_{11}O_4LaCp_2$ were studied. It was found that only in THF, it shows high activity, but in toluene and in ether it shows little activity, may be because the reaction time is too short.

$C_{10}H_{11}O_4LaCp_2$ can also catalyze the ethyl methacrylate polymerization (PEMA) and *t*-butyl methacrylate polymerization (PBMA). We get the polymers with high molecular weight and the narrow molecular distribution (Table-1).

Polymerization of MMA with different metal ions of $C_{10}H_{21}O_4LnCp_2$ was also

Polymerization of MMA with different metal ions of $C_{10}H_{21}O_4LnCp_2$ was also investigated (Table-2). The activities of $C_{10}H_{21}O_4LnCp_2$ decrease in the following order: $(La^{3+}) > (Pr^{3+}) > (Sm^{3+}) > (Dy^{3+})$ these orders are in agreement with the decreasing order of ionic radii, La^{3+}(1.061 Å) > Pr^{3+}(1.013 Å) > Sm^{3+}(0.964 Å) > Dy^{3+}(0.908 Å), similar to that found in $(C_5Me_5)_2Me(THF)_2$$^{1(b)}$ (Table-2).

According to the coordinating polymerization mechanism proposed by Yasuda$^{(1b)}$ (Scheme 1).

$C_{10}H_{21}O_4LaCp_2$ as a catalyst reacts with MMA, forming allyl alcohol lanthanide complexes with active ring it can initiate MMA polymerization, producing PMMA with high yield, narrow distribution. We may conclude that the initiating reaction is that the complexes attack —CH_2 group of MMA, forming Ln—O—$C(OCH_3){=}C(CH_3)_2$; the second MMA molecule reacts with it as a way of 1,4-Michael addition, producing an intermediate with active ring structure; the growth reaction is that the monomer attacks the growth end of active ring and gives out the matching ester group.

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