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POLYMERIZATION OF METHYL METHACRYLATE WITH ETHYLENE BRIDGED HETERODINUCLEAR METALLOCENE OF SAMARIUM AND TITANIUM—STUDY ON SYNERGISM AND KINETICS*

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Abstract: Comparison of MMA polymerization results with samarocene chloride, titanocene chloride and the title heterodinuclear (Sm-Ti) catalyst, respectively, showed synergism in the Sm-Ligand-Ti system, which obviously influenced the polymerization behaviors, for example, of yielding higher activity and higher molecular weight polymer. Kinetic studies on polymerization of MMA with ethylene bridged samarocene and titanocene chloride/$Al(i\text{-}Bu)_3$ showed that the polymerization rate was first-order on the catalyst concentration, and 1.9-order on the monomer. The overall activation energy measured was 52.8 kJ/mol.

Key words: heterodinuclear metallocene, heterodinuclear synergism, methyl methacrylate, polymerization, kinetics, titanocene, lanthanocene
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INTRODUCTION

Heterodinuclear complexes are of great importance for the study of the synergistic effects found in bimetallic catalysis (Adams, 1988; Reddy et al., 1989; Zheng et al., 1989; Werner et al., 1992), which indicated distinctive electronic, electrochemical and magnetic properties arising from the metal-metal interaction. Most of them were studied on the basis of theoretical calculation and spectroscopy, few were employed as polymerization catalysts (Mitani et al., 1995; Jerschow et al., 1995). At present, nearly all the research work remains at the stage of analysis of experimental phenomena and polymerization results. Studies of multicomponent catalytic system under homogeneous conditions proved the existence of catalytic effect enhancement compared to that of individual components. This enhancement effect is known as synergism (Hudeczek et al., 1992; Meyer, 1989). From the mechanistic point of view, synergistic effects have been postulated to occur on the basis of three ideas: (1) the M-L-M′ flexibility bridge permits the transfer of an atom or ligand from one metal center to the other; (2) an electronic cooperative effect can take place between metallic centers via orbital interactions with the bridging ligand; (3) steric influence of atoms and surrounding ligands may change the naked site of the active center.

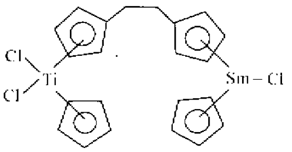

Fig.1 Structure of ethylene bridged samarocene and titanocene chloride

We reported (Sun et al., 2000) the polymerization results of methyl methacrylate with ethylene bridged samarocene and titanocene chloride alone or activated by $Al(i\text{-}Bu)_3$. As a continuation of this work, we studied the polymerization results with samarocene chloride and titanocene chloride respectively, in order to investigate the catalytic synergistic interaction between d-block element and f-block element. Ki-

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netic study of methyl methacrylate polymerization was also carried out.

EXPERIMENTAL DETAILS

Materials Methyl methacrylate was freed of inhibitor (by washing with diluted NaOH solution untill it became colorless), dried over calcium hydride, and distilled before use. Toluene was dried over sodium-benzophenone system. Ethylene bridged samarocene and titanocene chloride was synthesized from the corresponding monocyclopenta-dienyl compounds according to the literature (Chen, 1986). Al(i-Bu)$_3$ was purchased from Roth Company and used without further purification.

Polymerization Polymerization of MMA was carried out under a dry Argon atmosphere in a 20 ml ampoule. Certain amount of MMA and toluene was introduced into the ampoule by a syringe, then the polymerization was started by adding a toluene solution of catalyst with (or without) TIBA. The ampoule was immediately immersed in a temperature-controlled water bath. Polymerization was quenched by acidic ethanol and the polymer precipitated was dried at 40 ℃ under vacuum.

Measurement Molecular weight of PMMA was measured by an Ubbelohde-type viscometer in CHCl$_3$ at 30 ℃ and calculated with the following equation: $[\eta] = 4.3 \times 10^{-3} M_\eta^{0.8}$ (ml/g) (Zheng, 1986). Molecular weight distribution was determined by GPC (Waters Associate M730) at room temperature, using THF as a solvent and calibrated against the standard polystyrene.

RESULTS AND DISCUSSIONS

1. Synergism

Previous studies (Sun et al., 2000; Pan et al., 2000) indicated that single component lanthanocene complexes showed quite good catalytic efficiency for MMA polymerization at or above 60 ℃. The polymer yields together with some analytical results of polymerization are summarized in Table 1. Interestingly, lanthanocene catalysts easily produce high molecular weight PMMA ($M_\eta > 10^6$).

Table 1 Single component bulk polymerization of MMA with various lanthanocene catalysts

Catalyst	Temp. (℃)	Time (h)	MMA/Cat molar ratio	M_η ($\times 10^5$)	Mw/Mn	Yield (%)	Ref.
$O(C_2H_4CpCH_3)_2YI$	80	20	1000	15.7	2.06	83.2	Unpublished work
$O(C_2H_4CpCH_3)_2YCl$	80	20	1000	13.3	1.80	70.3	Sun et al.,2000
$Fc(OC_4H_8CpMe)(CpMe)YbCl$	60	25	1000	4.59	1.95	57.8	Pan et al.,2000
$Cp_2SmCl(\mu\text{-}C_2H_4)Cp_2TiCl_2$	60	20	1000	14.6	1.92	87.0	This work

Typical Ziegler-Natta catalysts are not very suitable for polymerizing polar monomers such as MMA, acrynitrile, etc., because the electron-donating atoms in monomers like oxygen and nitrogen have very strong tendency to coordinate with Ti and other similar transition metals, forming stable complex or destroying the catalytic ability. On the other hand, homogeneous group IV metallocenes activated by AlR$_3$ or MAO, sometimes using ZnEt$_2$ as an additive, were found to be able to initiate stereospecific polymerization of MMA, although not very efficiently.

GPC curves of typical PMMA catalyzed by the ethylene bridged metallocenes (shown in Fig.2) had one peak on the spectrum in the case

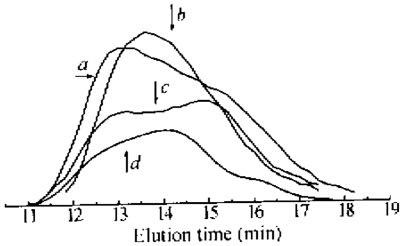

Fig.2 GPC curves of typical PMMA (Polymn. conditions: MMA/Cat. = 1000, 60 ℃, 20 h, bulk)
(a) 40 ℃, no Al; (b) 80 ℃, no Al; (c) Al/Cat. = 5; (d) Al/Cat. = 30

of single component catalysis, but two peaks if triisobutyl aluminum was used as cocatalyst. This suggested that the binary catalysis yielded two kinds of active species. The high molecular weight fraction is believed to be samarium initiated polymer, because it has similar elution time as that of PMMA produced in other polymerizations with various lanthanocene catalysts. The low molecular weight PMMA is caused by titanium /Al(i-Bu)$_3$. It should also be noticed that these two peaks on the GPC spectra can shift with the amount of Al(i-Bu)$_3$ added. This evidence excludes the possibility of alkyl aluminum as the initiator, because of the very narrow molecular weight distribution known in anionic polymerization.

The polymerization results of methyl methacrylate with Cp_2TiCl_2 are presented in Table 2. Run 1 shows the need for the cocatalyst, Al(i-Bu)$_3$, in the polymerization initiated by Cp_2TiCl_2. However, the binary catalyst was still not very efficient for MMA, and yielded only a relatively low molecular weight polymer. Its poor activity may be due to the "poisoning" of the catalyst. The carbonyl group of methyl methacrylates coordinates very easily with the electron deficient titanium ion. Such strong interaction makes the catalyst-monomer adduct too stable to initiate polymerization anymore.

Table 2 Polymerization results of methyl methacrylate with Cp_2TiCl_2

Run	MMA/Cp_2TiCl_2 molar ratio	Al(i-Bu)$_3$/Ti molar ratio	Temp.(℃)	Time(h)	Conv.(%)	M_η($\times 10^4$)
1	2000	–	40	18	0	0
2	2000	10	40	18	16	6.34
3	2000	20	40	18	26	4.47
4	2000	30	40	18	21	2.67
5	2000	40	40	18	26	1.66
6	2000	30	60	18	25	5.24
7	2000	30	80	18	42	4.83
8	500	30	40	18	33	0.34
9	1000	30	40	18	28	4.70
10	4000	30	40	18	17	3.53

Table 3 shows bulk polymerization results and the possibility of samarocene chloride as an initiator. With or without Al(i-Bu)$_3$, Cp_2SmCl can promote the polymerization, producing high molecular weight ($M_\eta > 10^5$) PMMA. Both the polymerization rate and the monomer conversion increased with temperature. Addition of Al(i-Bu)$_3$ intensified the catalytic activity. The monomer conversion reached 72.4% at Al/Sm = 15 after 20 hours compared to 40.7% without Al(i-Bu)$_3$. For better comparison of the synergistic effects on the polymerization, results of several other lanthanocene catalysts are also summarized in Table 3 (Sun et al., 2000; Pan et al., 2000). From the data, it can be seen that ethylene bridged samarocene and titanocene (Run 23, 24, 25) showed better activity than both alone, confirming the existence of synergistic effects. Since Sm(III) has a smaller electronegativity than Ti(IV), the electron cloud of the samarocene part may shift toward the titanocene part and lower the Lewis acidity of the titanium cation. It makes titanocene more tolerable to polar molecules. In addition, the electron deficiency of samarocene would benefit the coordination of methyl methacrylate, and lead to the production of high molecular weight PMMA.

2. Kinetics

At very low conversion condition, in order to derive the rate of polymerization, the steady-state assumption is made that the concentration of active species increases initially, but almost instantaneously reaches a constant steady-state value. The rate of change of the concentration of active species quickly becomes and remains at zero during the course of the polymerization. Therefore, the rate of monomer disappearance, which is in fact the rate of polymerization, is given by

$$\frac{-\mathrm{d}[M]}{\mathrm{d}t} = R_i k + R_p \approx R_p = K_p[C]^m[M]^n$$
$$= K[M]^n \qquad (1)$$

where R_i and R_p are the rates of initiation and propagation, respectively. However, the number of molecules reacting in the initiation step is far less than that in the propagation step. To a very close approximation the former can be neglected and the polymerization rate is simply expressed as the rate of propagation. In the Eq. (1), $[M]$ is the concentration of monomer and $[C]$ is the total concentration of active species, namely all growing chains.

Table 3 Bulk polymerization results of methyl methacrylate with Cp_2SmCl

Run	MMA/Cp_2TiCl_2 molar ratio	$Al(i\text{-}Bu)_3/Ti$ molar ratio	Temp.(℃)	Time(h)	Conv.(%)	$M_\eta(\times 10^4)$
11	1000	–	40	20	15.2	3.71
12	1000	–	80	15	43.8	3.16
13	2000	–	60	20	25.5	4.88
14	500	–	60	20	64.1	1.81
15[e]	1000	–	60	20	21.9	2.37
16	1000	–	60	20	40.7	3.38
17	1000	5	60	20	53.0	3.46
18	1000	15	60	20	72.4	2.02
19[f]	1000	15	60	20	49.8	2.69
20[a][12]	1000	–	80	20	70.3	13.3
21[b][13]	1000	–	60	20	52.5	7.38
22[c][13]	1000	–	60	20	57.8	4.59
23[d]	500	–	60	20	97.6	13.7
24[d]	1000	–	60	20	87.0	14.6
25[d]	2500	–	60	20	59.5	16.1
26[d]	1000	5	60	10	52.4	2.95

a: catalyst as $O(C_2H_4CpCH_3)_2YCl$; b: $(MeCp)_2YbCl$; c: $Fc(OC_4H_8CpMe)(CpMe)YbCl$; d: the titled heterodinuclear catalyst Sm-Ti; e, f: polymerization in toluene solution (MMA/Tol. = 1/1)

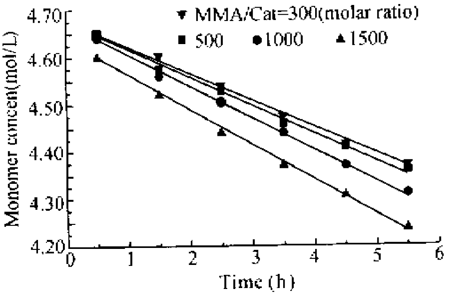

Fig.3 Relationship of monomer conversion and time (polymerization conditions: 60 ℃, Al/Cat = 5)
▼: MMA/Cat = 300(molar ratio) ■: 500 ●: 1000 ▲: 1500

Taking logarithms of both sides leads to the useful expression.

$$\log R_p = \log K + n\log[M] \qquad (2)$$

Reading the data of R_p from the plots of $[M]([M] = [M]_0(1 - p))$ vs polymerization time, (see Fig.3) where $[M]_0$ means the initial monomer concentration and p means the conversion ratio of monomer. R_p is easily found from the slope of a certain date point on the curve. If Eq.(2) is correct, one will get a linear plot of $\log R_p$ vs. $\log[M]$ with slope = n, where n represents the reaction order of monomer concentration.

As shown in Fig.4, $\log R_p$ is directly proportional to $\log[M]$. The obtained average of n as 1.9 ± 0.25 indicates a 1.9-order dependence on monomer concentration. A fractional reaction order usually hints a complicated transition state existed during the recombination of atoms, and indicates that polymerization of MMA with the heterodinuclear catalyst was not as simple as coordination, insertion and chain propagation. However, synergistic interaction may occur in the transition state.

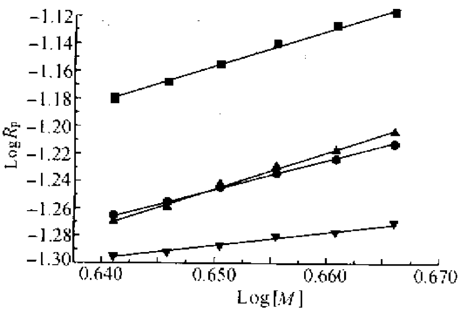

Fig.4 Relationship of logR_p and log[M] (polymerization conditions: same as in Fig.2)

The intercept of the linear plot yields the value of log$K$, where $\log K = \log K_p + m\log[C]$. Thus the reaction order of [C] can be determined from the plot of log$K$ vs. log[C] in Fig.5. Since the slope, $m = 1.13 \pm 0.04$, it results in a first-order dependence of the polymerization rate on catalyst concentration. Substitution of the value of m, n into Eq.(1) yields the overall equation of polymerization rate as

$$R_p = K_p[M]^{1.9}[C] \qquad (3)$$

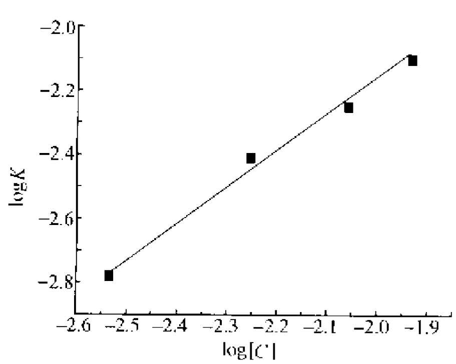

Fig.5 Relationship of log$K$ and log[C]

Fig.6 and Fig.7 show the relationships of monomer conversion and time, at different temperature, respectively. The effect of polymerization temperature on the chain propagation rate is shown in Fig. 8. Calculated with Arrhenius equation, the activation energy of propagation is about 52.8 kJ/mol, which is higher than that of other lanthanide catalysts, such as 32.1 kJ/mol of Y(acac)$_3$-n-BuMgCl (Sun et al., 1997) and 33 kJ/mol of Nd(P$_{507}$)$_3$-Al(i-Bu)$_3$ (Zhang et al., 1994) for MMA polymerization. The higher activation energy is probably due to the fact that monomer molecules in the polymerization process must overcome more steric hindrance of heterodinuclear catalyst to coordinate with it's active centers than those in mononuclear catalysis. Since chain propagation is realized on both two metals simultaneously, it is easy to understand why the heterodinuclear complex has better catalytic activity than either of its moiety.

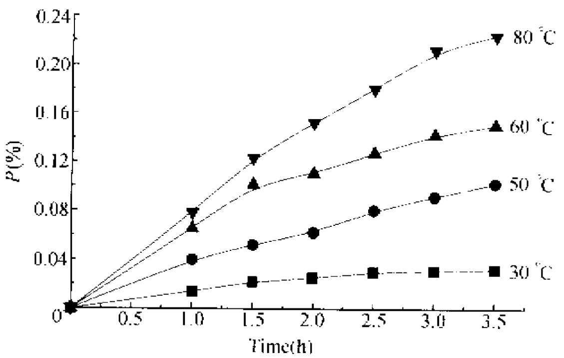

Fig.6 Relationship of conversion and time at different temperature (polymerization conditions: MMA/Cat. = 1000, Al/Cat. = 5)

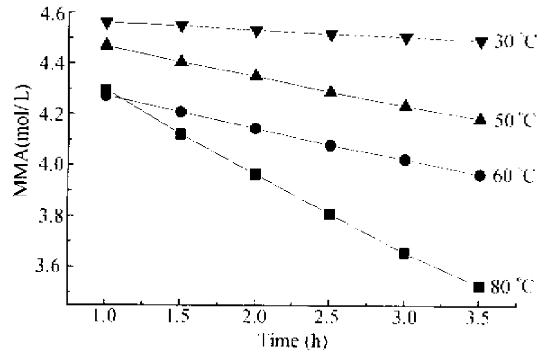

Fig.7 Relationship of [MMA] and time (polymerization conditions: same as Fig.5)

CONCLUSIONS

MMA polymerization results with samarocene chloride, titanocene chloride and the title het-

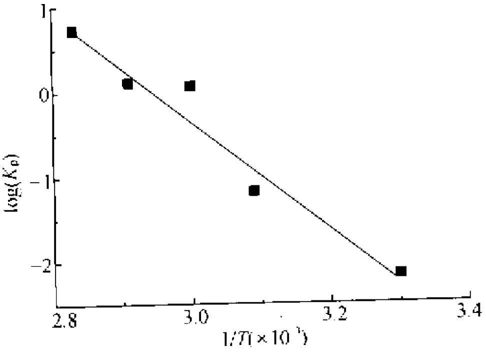

Fig.8 Relationship of $\log K_p$ and $1/T$

erodinuclear catalyst showed synergism in the Sm-Ligand-Ti system，which resulted in higher activity and higher molecular weight polymer. Kinetic studies of the polymerization of MMA with ethylene bridged samarocene and titanocene chloride/$Al(i\text{-}Bu)_3$ were investigated. The polymerization rate was first-order on the concentration of catalyst and a fractional order on the monomer concentration. The overall activation energy was measured as 52.8 kJ/mol.

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