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# POLYMERIZATION OF METHYL METHACRYLATE WITH IRON-YTTERBIUM DINUCLEAR METALLOCENE CATALYST*

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**Abstract**: A novel iron-ytterbium dinuclear catalyst, FcB(MeCp)Yb (MeCp) Cl (Fc: ferrocenyl, B: diethylene ether), was synthesized for the polymerization of methyl methacrylate (MMA). Synergistic effects between the ferrocenyl group and the lanthanocene part were investigated regarding their catalytic behaviors. UV, IR, GPC and NMR were used to characterize the structures of the catalyst and polymer. Kinetic study showed that polymerization is first order in monomer concentration and fractional order (0.78) in the catalyst. The bimetallic complex is a good catalyst for the polymerization of MMA, giving high molecular weight PMMA with 78% syndiotacticity.

**Key words**: heterodinuclear catalyst, synergistic effect, lanthanocene, kinetics, polymerization, MMA
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## INTRODUCTION

Heterodinuclear complexes are of great interest for the study of synergistic effects found in bimetallic catalysis (Dombek, 1985; JünLing et al., 1993; Mccollum et al., 1996). More and more synthetic routes have been reported in the last decade (Harter et al., 1989; Scott et al., 1993; Diamond et al., 1994; Reddy, 1989; Nifant'ev et al., 1992), but few of those were employed as polymerization catalysts (Jerschow et al., 1995; Mitani et al., 1995; Diamond et al., 1996). Weak and too complicated interaction between different metal atoms hinders deeper research on synergism. Up to now, there is no consensus on a detailed and complete theory on synergism.

The homogeneous catalyst system based on metallocene is currently regarded as one of the greatest discoveries in polymer science after the Ziegler-Natta catalyst. It is assumed that the active center is a single metal cation with a defined structure. Present studies on metallocene catalysts mainly focus on the polymerization of nonpolar monomers, such as olefins, dienes, etc. Recently, however, it was found that group $IV_B$ metallocene alkyls and lanthanocene hydrides are good catalysts for the polymerization of methyl methacrylate.

Bridged bis (cyclopentadienyl) ligand systems containing two metal centers are appropriate for use to examine the synergistic effects because both of its metal sites are in close proximity. Ferrocene, which possesses typical aromatic properties, is selected as the initial material to synthesize a novel heterodinuclear metallocene.

This paper reports the preliminary results of polymerization of MMA with catalyst (I).

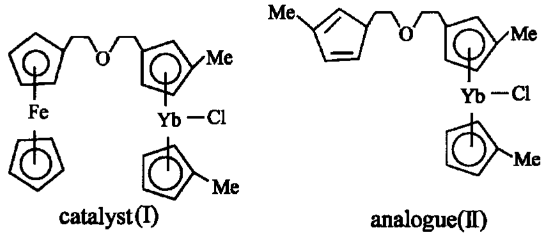

**Fig. 1 Structure of heterodinuclear catalyst and analogue**

## EXPERIMENTAL SECTION

**Materials**: MMA was washed with diluted NaOH until it became colorless, dried over anhydrous $MgSO_4$, then distilled over $CaH_2$ under reduced pressure and then stored in a refrigera-

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tor. Toluene was refluxed over blue benzophenone-Na complex. Catalyst (I), $MeCpYbCl_2$ and ferrocene were prepared according to literature(Mitani et al., 1996; Chen, 1986).

Analogue (II) was prepared as follows. To a solution of diethylene ether bridged bis(methylcyclopentadiene) (50 mmol) in THF (150 ml) was added n-BuLi (42.9 ml, 60 mmol) with ice-salt bath; after which, the solution was warmed to room temperature, and stirred for 10 hours. The reaction mixture was added dropwise to a solution of $MeCpYbCl_2$ (50 mmol) in THF (50 ml) and stirred overnight. After filtration of the solid, the clear solution was concentrated and washed with hexane, to yield an orange powder (6.8 g, 27% conversion).

**Polymerization:** Under Argon protection, the catalyst was dissolved in MMA. The mixture was aged for fifteen minutes at 40 ℃ and was occasionally shaken.

The polymerization was performed in a 25 ml ampoule, which was baked, vacated and purged with dry Argon before use. Monomer and catalyst solutions were introduced successively into the ampoule by using a syringe. Then the ampoule was placed in a water bath at constant temperature for a defined time. Polymerization was terminated by adding 2 ml ethanol containing 5% hydrochloric acid, and the polymer was precipitated by using a large amount of ethanol, filtered, purified in chloroform-ethanol, and finally dried at 50 ℃ under vacuum.

**Measurements:** The intrinsic viscosity of PMMA was measured at 30 ℃ by Ubbe-lodhe viscometer, using chloroform as solvent, and calculated according to the following equation (Zheng, 1986).

$$[\eta] = 4.3 \times 10^{-3} \bar{M}_\eta^{0.8} \quad (\text{ml/g}) \quad (1)$$

and the polymer molecular weight distributions were determined at 30 ℃ with a gel permeation chromatogram (Waters Associates-M730) in THF, using standard polystyrene for calibration. The microstructure of PMMA was investigated in $CDCl_3$ by $^1$HNMR at ambient temperature recorded on Jeol - 90Q NMR spectrometer, using TMS as internal standard. The resonance peaks of $CH_3$ at 0.92, 1.02, 1.20 indicated syndiotactic (s), atactic (h), and isotactic (i) structure respectively. IR spectra were recorded on Nicolet - M560, using ATR (Attenuated Total Reflectance) method. UV absorbance of catalysts was observed on a Beckmann Du - 50 spectrophotometer.

## RESULTS AND DISCUSSION

### 1. Polymerization behaviors

MMA can be polymerized by many methods, such as free radical, anionic, cationic, coordination, GTP (Group Transfer Polymerization), ATRP (Atom Transfer Radical Polymerization) (Liu et al., 1995; Webster et al., 1983; Wang, 1995), and so on. In a previous paper, we reported that polar monomers such as ε-caprolactone and methyl methacrylate can be polymerized by lanthanocene chloride without any cocatalyst (Sun et al., 1998). In this paper, further work is described. Single-component catalyst, heterodinuclear lanthanocene (I), was successfully applied in the polymerization of MMA.

The effect of the molar ratio [MMA]/[cat.] is shown in Fig. 2. With the increase of catalyst amount, the monomer conversion rises gradually and reaches a peak value at [MMA]/[cat.] = 500. However, the molecular weight of polymer has an optimal ratio of 3000, at which super high molecular weight PMMA ($1.04 \times 10^6$) is produced.

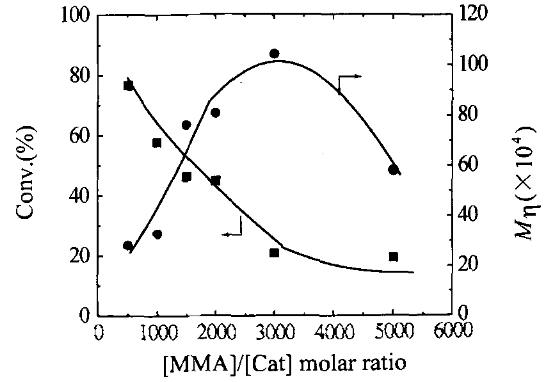

**Fig.2** **Effect of molar ration [MMA]/[cat]**
Polymn. conditions: 60 ℃, bulk, 25h

The dependence of molecular weights of PMMA on polymerization time is shown in Fig. 3. Polymerization degrees (DP) of PMMA measured by GPC remained constant, even if samples were taken out from the ampoule during polymerization.

Temperature plays an important role in the polymerization, as shown by the results listed in Table 1. The conversion at 0 ℃ was rather low and only some oil-like oligomers were obtained. Raising temperature increased polymerization rate. But monomer escape was also enforced by overheat as well as chain transference. The catalyst showed better activity at 30 ℃.

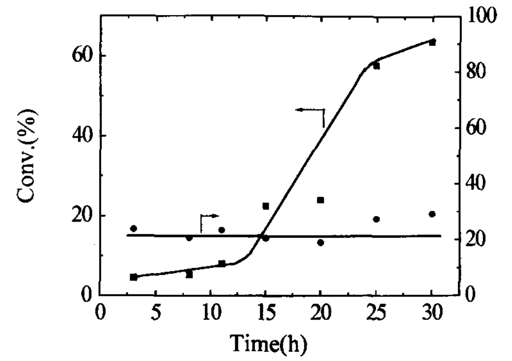

**Fig. 3 Effect of polymerization time**
Poylmn. conditions: [MMA]/[cat] = 1000, 60℃, bulk

**Table 1. Effect of temperature on the polymerization**

| Temp (℃) | 0℃ | 30℃ | 60℃ | 80℃ |
|---|---|---|---|---|
| Yield (%) | 3.2 | 84.3 | 57.8 | 31.1 |
| MW (×$10^4$) | / | 66.8 | 32.8 | 20.5 |

Polymn. conditions: [MMA]/[cat] = 1000, bulk, 25h

$AlR_3$ is a common cocatalyst in the Ziegler-Natta system. When catalyst (I) was treated with $Al(i\text{-}Bu)_3$, as expected, it became more active and yielded PMMA with 74.8% conversion at 40℃ for 10 hours. To our amazement, these products were insoluble in chloroform, which were never found to be the case before. GPC analysis of the THF-soluble part showed that the polymer MWD was as narrow as 1.81, and the number-average molecular weight was $1.11 \times 10^5$.

To investigate the function of the ferrocenyl group, an analogue was synthesized (shown in Fig. 1). Polymerizations of MMA carried out with a mixture of analogue (II) and ferrocene at various ratios (listed in Table 2) showed that analogue (II) was also efficient at 60℃, having nearly equal activity, but it was not very good at 30℃. This behavior was also noted in the catalyst $O(C_2H_4)_2(MeCp)_2YCl$ we studied before (Sun et al., 1998). In contrast, catalyst (I) was much more active at low temperature. It seems that the distinctive property should be attributable to the intrinsic character of the heterodinuclear complex. From the viewpoint of steric hindrance, the analogue is similar to catalyst (I), so it should not derive from the steric effect of ferrocene. Why adding ferrocene could promote the polymerization is not clear. On the typical GPC spectrum of PMMA catalyzed by the mixture (Fig.4), there is only one peak, suggesting that only one active species exists in the system. For comparison, the UV Spectra of catalyst (I), analogue (II) and ferrocene are given

**Table 2 Effect of the ferrocenyl group on polymerization**

| Molar ratio Fc/cat(II) | Only cat(II) 30℃ | Only cat(II) 60℃ | 50/1 | 10/1 | 1/1 | Only ferrocene |
|---|---|---|---|---|---|---|
| Yield (%) | Trace | 52.5 | 47.4 | 3.95 | 3.37 | No polymer |
| MW(×$10^4$) | / | 73.8 | 33.7 | 21.9 | 22.2 | / |

Polymn. conditions: [MMA]/[cat (II)] = 1000, bulk, 30℃, 25h

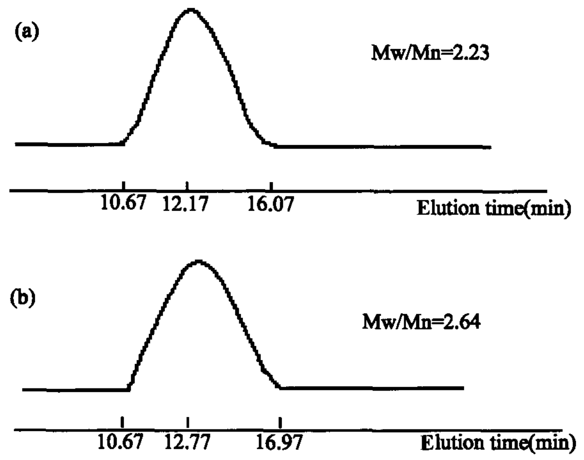

**Fig. 4 GPC spectra of PMMA**
(a) catalystI. (Fe-Yb) (b) analogue. II + Ferrocene

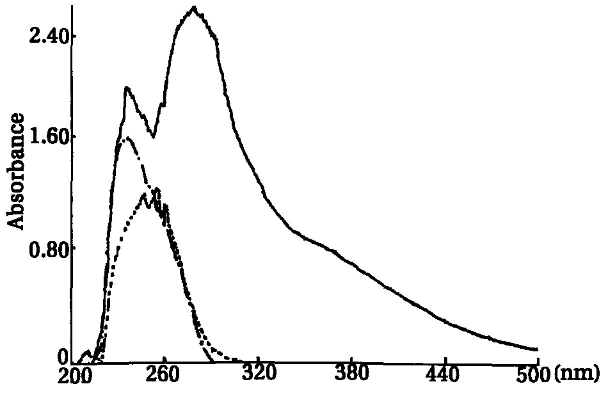

**Fig. 5 UV Spectra of catalysts**
—·— Ferrocene ······ analogue(II) ——catalyst(I)

in Fig. 5, showing clearly that there is obvious electronic interaction between iron and ytterbium atoms. The absorption peak of analogue (II) shifts from 250 nm to 280 nm when it was combined with the ferrocenyl group. The bathochromic shift indicates that ferrocene has strong conjugation effect (Chen, 1981). Based on the above evidences, we propose the main function of ferrocenyl is to stablize the active center, not to initiate the polymerization.

The IR spectrum is a powerful tool not only for determining the structure of a compound, but also for studying its stereo conformation. Syndiotacticity of polymer can be measured by comparison of the transparencies at 1063 and 1393 $cm^{-1}$ (Shen, 1982). PMMA catalyzed by heterodinuclear lanthanocene at 30℃ is mainly syndiotactic, 81% on IR spectrum (Fig. 6), and 77.8% on $^{1}HNMR$ spectrum (Fig. 7).

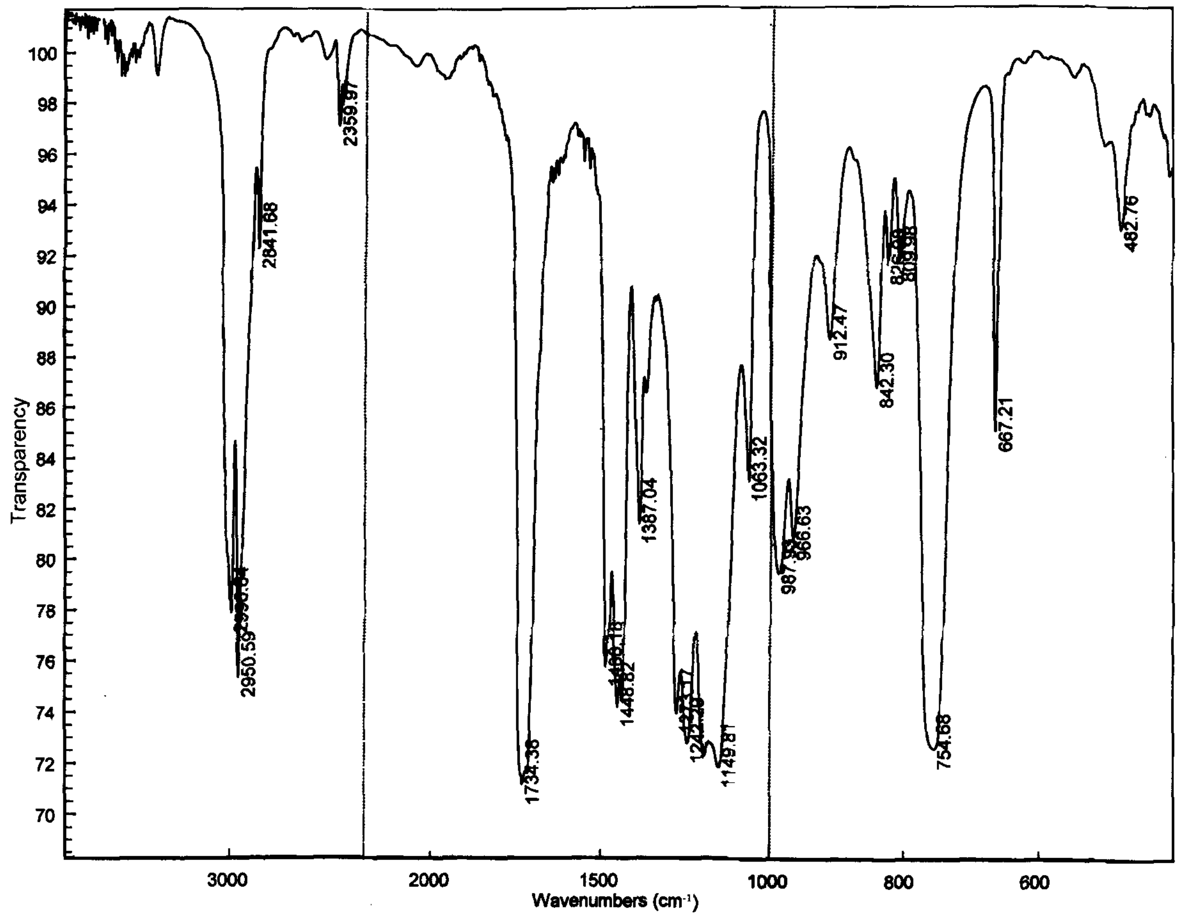

Fig. 6 IR spectrum of PMMA

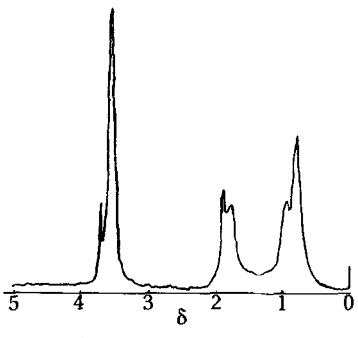

Fig. 7 1HNMR spectrum of PMMA

Catalyst (I) dissolves very easily in monomer. From the IR spectrum of the MMA solution (Fig. 8), the absorption peak of the carbonyl group at 1736.4 $cm^{-1}$ splits into a peak at 1747.9 $cm^{-1}$ and one at 1738.5 $cm^{-1}$, demonstrating the coordination reaction between the ester carbonyl group and the ytterbium atom.

## 2. Kinetic study of MMA polymerization

The kinetics of MMA polymerization with heteronuclear lanthanocene at 60℃ was also inv-

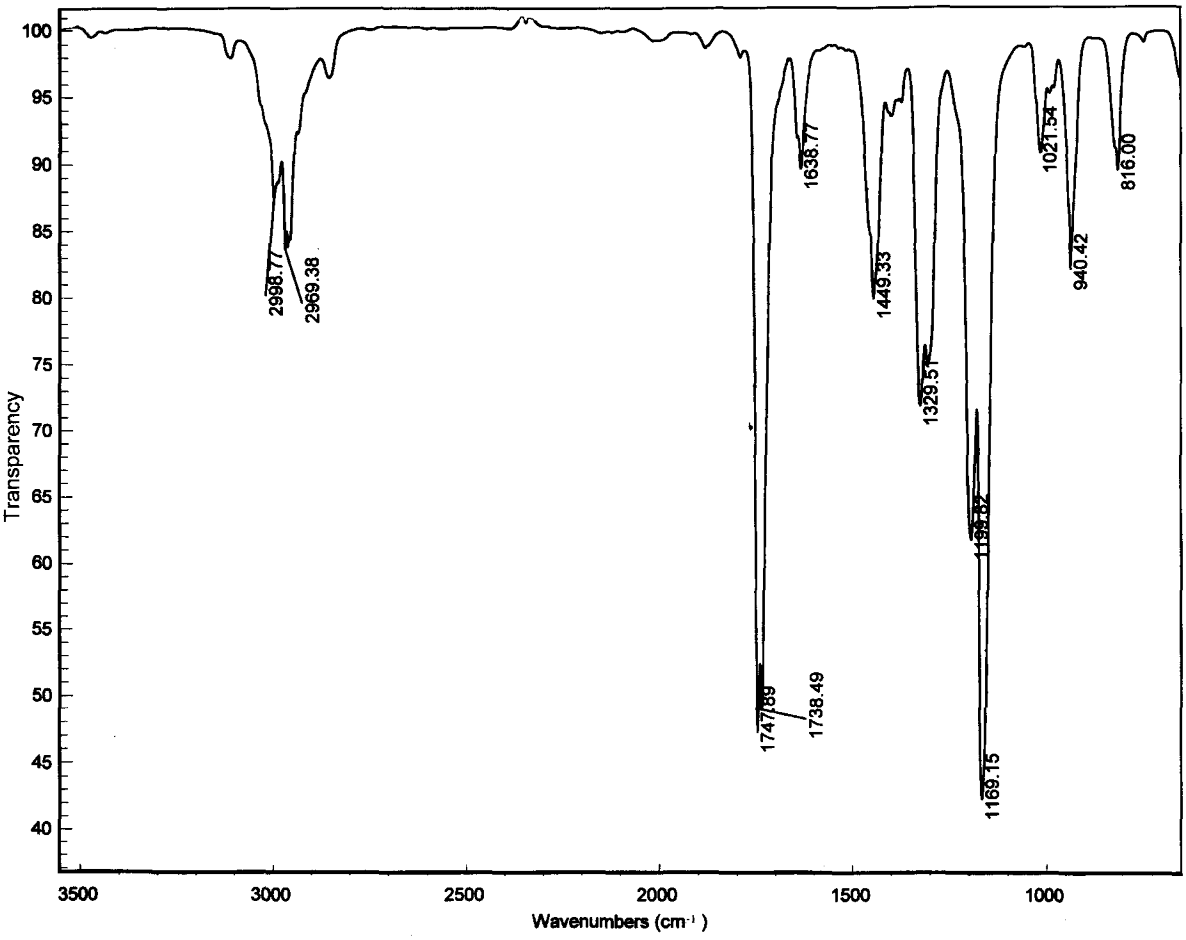

**Fig. 8 IR spectrum of catalyst (I) in MMA**

estigated. The linear plots of $\ln([M]_0/[M])$ versus $t$ (time) indicate that the polymerization is first order in monomer concentration (shown in Fig. 9). The fractional order, 0.78, in catalyst (I) was also obtained from the slopes of the plots in Fig. 10. Therefore, the polymerization of methyl methacrylate catalyzed by catalyst (I) proceeds according to a simple overall kinetic law as described by Equation 2.

$$R_p = -d[\mathrm{MMA}]/dt = k[\mathrm{MMA}][\mathrm{cat}]^{0.78} \qquad (2)$$

Generally, the polymerization of MMA shows fractional or higher (close to 2) order in the catalyst if the catalyst aggregates in the polymerization solution (Duda, 1990; Ouhadi et al., 1976). The kinetic equation shows that, under the polymerization conditions, catalyst (I) is probably dimeric through a chlorine bridge, which is a very common structure in lanthanocene compounds (Xie et al., 1998).

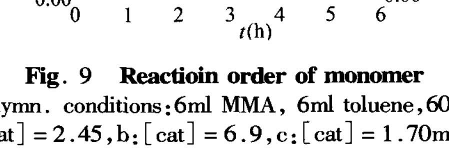

**Fig. 9 Reactioin order of monomer**

Polymn. conditions: 6ml MMA, 6ml toluene, 60℃
a: [cat] = 2.45, b: [cat] = 6.9, c: [cat] = 1.70mmol/l

The energy of activation ($E_a$) is calculated from the slope of the Arrhenius formula plotted in Fig. 11. It is about 24 kJ/mol. The value is in the same range of magnitude as that of other known rare earth coordination catalysts for MMA (Zhang et la., 1994).

The results of investigation of chain termin-

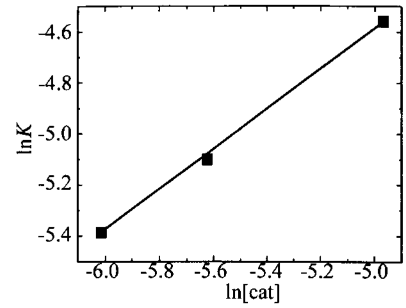

**Fig. 10 Reaction order of catalyst**

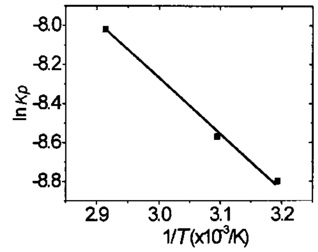

**Fig. 11 $E_a$ from Arrhenius formulation**

ation is shown in Fig. 12. If the termination reaction is a single molecular process, it should obey the following equation, yielding linear plots of $\ln(\ln([M]_0/[M])) \sim t$.

$$[\text{cat}] = [\text{cat}]_0 e^{-k_i t} \qquad (3)$$

$$R_p = \frac{-d[M]}{dt} = k_p[M][\text{cat}]^{0.78} = k_p[M]([\text{cat}]_0 e^{-k_i t})^{0.78} \qquad (4)$$

$$\ln(\ln[M]_0/[M])) = A - 0.78k_i t \qquad (5)$$

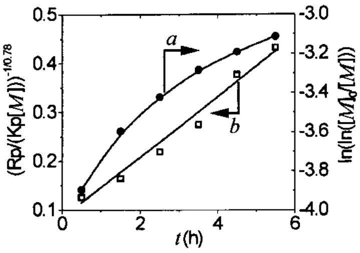

**Fig. 12 Investigation of chain termination**

a: single molecular termination $\ln(\ln[M]_0/[M])) \sim t$

b: bimolecular termination $(Rp/Kp[M])^{-1/0.78} \sim t$

However, if it is a bimolecular mechanism, with the same treatment, the equation can be written as:

$$R_p = \frac{d[M]}{dt} = k_p[M]\left(\frac{[\text{cat}]_0}{1 + k_i[\text{cat}]_0 t}\right)^{0.78}$$

$$\left(\frac{R_p}{k_p[M]}\right)^{-1/0.78} = \left(\frac{[\text{cat}]_0}{1 + k_i[\text{cat}]_0 t}\right)^{-1}$$

$$\left(\frac{R_p}{k_p[M]}\right)^{-1/0.78} = B + k_i t \qquad (6)$$

and $(R_p/k_p[M])^{-1/0.78}$ will show linear relationship with $t$. From Fig. 12, the deactivation of active centers should be a bimolecular termination.

## CONCLUSION

Novel heterodinuclear complexes were synthesized for methyl methacrylate polymerization. The bridged bis(Methylcyclopentadienyl) ligand offers a synergistic effect owing to the electronic and/or steric interaction between each part during the polymerization. Therefore, the heterodinuclear Fe-Yb complex exhibits catalytic behavior distinctly different from that of mononuclear and homodinuclear complexes because of the conjugation effect of ferrocene. Kinetic studies indicate that the polymerization system has a small active energy.

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