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Novel $MgCl_2$-supported catalyst containing diol dibenzoate donor for propylene polymerization

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Abstract

A novel $MgCl_2$-supported Ziegler–Natta catalyst containing 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate donor for propylene polymerization was studied, and compared with catalysts with different internal donors, such as benzoate, phthalate and diether, in polymerization dynamic behavior, activity, hydrogen response and stereospecificity. It was found that there are two highly isospecific active sites in the catalyst with dibenzoate internal donor system and the effections of temperature are different on the performances of the two highly isospecific sites.

Keywords: Polypropylene; Catalyst; Diol dibenzoate

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1. Introduction

Electron donors play a fundamental role in modern Ziegler–Natta catalyst systems for propylene polymerization [1]. As we know, the internal donor of the third generation Ziegler–Natta catalyst system for propylene polymerization is benzoate, e.g. ethyl benzoate, and its activity and stereospecificity are much lower than those of the fourth generation catalyst with phthalate as internal donor [1]. A number of other Lewis bases such as diether [2,3] and succinate [4] have been developed as internal donors for catalyst in recent years. Generally, the performance of catalyst with different internal donor appears to improve in the following order [5,6]:

Activity: Benzoate < Succinate ≈ Phthalate < Diether
Isotacticity: Benzoate < Diether ≈ Phthalate < Succinate
Hydrogen response: Succinate < Phthalate < Diether
The molecular weight distribution of obtained polymer: Diether < Phthalate < Succinate

External donor also plays an important role in catalyst performance. For catalyst with benzoate, phthalate or succinate as internal donor, external donor is required to achieve acceptable isotacticity of obtained polypropylene, though external donor is not applied to catalyst with diether as internal donor, which may be caused by the difficulty in removing diether from the catalyst solid with alkyl aluminium [2–8].

In the paper, we used our newly developed diol dibenzoate [9,10] 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate (IAIPPDB) as internal donor (ID) to prepare a catalyst for propylene polymerization with hydrogen as chain transfer agent, and compared its performance with that of catalyst with ethyl benzoate, dibutyl phthalate, or diether as internal donor. The structures of 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate and diether 2-isoamyl-2-isopropyl-1,3-dimethoxypropane (IAIPDMP) are shown in Fig. 1.

2. Experimental part

2.1. Materials

Cyclohexanemethyl dimethyloxy silane (CHMDMS) was dried over 4A molecular sieves. Triethylaluminium (Ethyl Co., 95% purity) was used without further purification.

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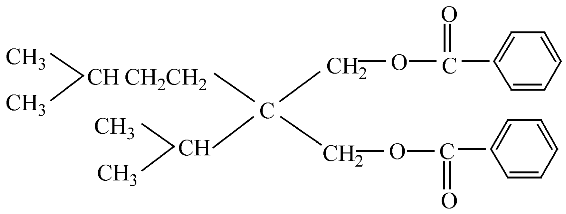
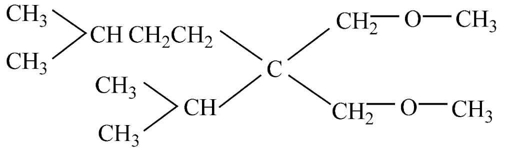


IAIPPDB



IAIPDMP

Fig. 1. Structures of 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate (IAIPPDB) and 2-isoamyl-2-isopropyl-1,3-dimethoxypropane (IAIPDMP).

Propylene (Yanshan Petrochemical Co., polymerization grade) was dried by passing through 4A molecular sieve column.

2.2. Preparation of the catalyst

To a reactor were added successively 4.8 g magnesium chloride, 95 ml toluene, 4 ml epoxy chloropropane, and 12.5 ml tributyl phosphate. The mixture was heated to 50 °C with stirring and held at the temperature for 2.5 h, then added 1.4 g phthalic anhydride and held at the temperature for one more hour. The solution was cooled to below − 25 °C and added dropwise 56 ml $TiCl_4$ before heated slowly to 80 °C, then added 5 mmol of internal donor to the system and the reaction was held at the temperature for 1 h. After supernatant removed, the residue was washed with toluene. The resulting solid precipitate was treated twice with 60 ml toluene and 40 ml $TiCl_4$ at 100 °C for 2 h. After the supernatant removed, the residue was washed with toluene and hexane to yield the solid catalyst.

2.3. Polymerization

2.3.1. Bulk polymerization

Procedure for bulk propylene polymerization was as follows: to a 5 l stainless steel autoclave, which had been replaced with propylene gas completely, 2.5 mmol $AlEt_3$, 0.1 mmol external donor, approximately 10 mg of the solid catalyst and 2.4 l hydrogen were added, followed by introduction of 2.3 l liquid propylene. The reactor was heated to reaction temperature, and the polymerization was performed at that temperature for 1 h. After that the temperature was reduced, the pressure relieved, and PP fluff was obtained.

2.3.2. Slurry polymerization

The slurry polymerization of propylene was carried out at constant pressure and temperature in a 1 l glass reactor equipped with a thermostatic system and a turbine stirrer. Decane was used as reaction medium. The reactor was cleaned and filled with monomer. The reactor was charged with 200 ml decane and its temperature raised to 70 °C. The compound of catalyst (40 ~ 50 mg), required amount of $AlEt_3$ (Al/Ti = 150) and cyclohexanemethyl dimethyloxy silane (CHMDMS), was injected into the reactor under 0.125 MPa of monomer and then the polymerization started. The reactor temperature and pressure were maintained constant within ± 0.2 °C and ± 0.002 Mpa, respectively. The stirring speed was 1000 rpm in order to eliminate the effects caused by monomer diffusion through the gas–liquid interface. The polymerization rate was determined by measuring the rate of monomer consumption with a mass-flow meter.

2.4. Characterization

The isotacticity index (II) of polymer was obtained by boiling heptane extraction for 6 h.

^{13}C NMR analysis was performed in the following manner. The polymer solution was prepared by dissolving 500 mg of the heptane insoluble polymer sample in 0.5 cm^3 *o*-dichlorobenzene-d_4 at 110 °C. The ^{13}C NMR spectrum was recorded on a Bruker DMX400 spectrometer operating at 100 MHz under proton noise decoupling in Fourier-transform mode. Instrumental condition was as follows: pulse angle 90°; pulse repetition 2 s; spectral width 180 ppm; scans ca. 25,000; temperature 383 K; data points 64 K.

The molecular weight and its distribution (MWD) of the polypropylene were determined by a Waters Alliance GPCV2000 gel permeation chromatograph (GPC) equipped with a refractive index detector, using three Polymer Laboratory MIXED-B columns and 1, 2, 4-trichlorobenzene as solvent at 150 °C. The number-average and weight-average molecular weight (M_n and M_w, respectively) values were evaluated with reference to a polystyrene standard calibration.

The melting temperature (T_m) was measured on a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) in the following manner. First, the sample was heated to 210 °C at 10 °C/min and maintained at this temperature for 5 min in order to remove the thermal history. Then, it was cooled to 50 °C at 10 °C/min, followed by reheating at 10 °C/min. The thermogram of each sample was recorded in the second heating run.

3. Results and discussion

The performances of catalysts with different internal donors with or without external donor are shown in Table 1.

Table 1
The performances of catalysts with different internal donor

Run	Catalyst	Internal Donor	External Donor	Activity kgPP/gcat	Isotacticity Index %	M_w 10^4	MWD
1	Cat-A	EB	CHMDMS	5.6	94.5	35.1	7.8
2	Cat-B	IAIPDMP	CHMDMS	54.3	98.8	30.2	4.6
3	Cat-B	IAIPDMP	no	60.4	98.4	28.9	4.8
4	Cat-C	DNBP	CHMDMS	40.3	98.5	34.8	5.2
5	Cat-C	DNBP	no	32.8	89.2	–	–
6	Cat-D	IAIPPDB	CHMDMS	52.1	98.6	70.6	7.4
7	Cat-D	IAIPPDB	no	49.2	96.6	77.3	10.7

Polymerization: bulk, 70 °C, CHMDMS/$AlEt_3$ = 0.04.

The activity of Cat-D with dibenzoate (IAIPPDB) as internal donor is higher than that of Cat-C with phthalate (DNBP) or Cat-A with benzoate (EB) as internal donor, but lower than that of Cat-B with diether (IAIPDMP) as internal donor. The molecular weight distribution of obtained polymer by Cat-D is wider than that by Cat-C or Cat-B. As we know that the hydrogen concentration and the hydrogen response are the key factors that affect the molecular weight of obtained polymer, polymer with higher molecular weight can be obtained by using a catalyst with poorer hydrogen response at the same hydrogen concentration. Table 1 shows that the molecular weight of obtained polymer by Cat-D is much higher than that by Cat-A, Cat-C or Cat-B, which indicates that the hydrogen response of catalyst with IAIPPDB as internal donor is poorer than that of catalyst with EB, DNBP or IAIPDMP as internal donor; the isotacticity index (II) of polymer obtained by Cat-D with CHMDMS is similar to that obtained by Cat-B and Cat-C with CHMDMS and the isotacticity of polymer obtained by Cat-D without external donor is lower than that obtained by Cat-B, but much higher than that obtained by Cat-C. The methyl regions of ^{13}C NMR spectra of heptane insoluble fractions of polypropylene obtained by catalyst with different donor are shown in Fig. 2, and the detailed data are shown in Table 2. The [mmmm] obtained by Cat-D with CHMDMS is higher than that by Cat-A, Cat-B and Cat-C, which imply that the catalyst with IAIPPDB as internal donor has high isospecificity. It also can be found that the Cat-D without external donor still has high isospecificity, of which the performance is similar to that of Cat-B [2,11]. As

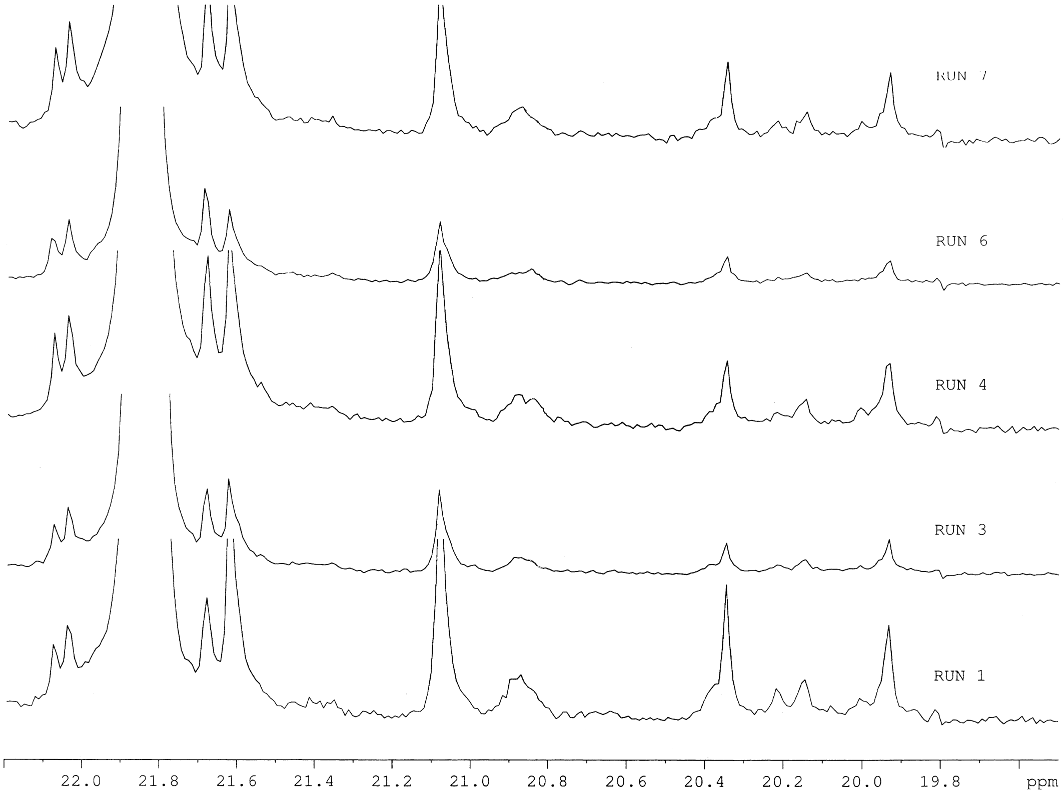


Fig. 2. The methyl regions of ^{13}C NMR spectra of heptane insoluble fractions of polypropylene obtained by catalyst with different donor. Polymer is as described in Table 1.

Table 2
Pentad sequence distributions of heptane insoluble fraction of polymers (in %)

polymer	mmmm	mmmr	mmrr	mrrm + mmrm	rrrr	mrrr	mrrm
Run 1	85.9	5.7	3.0	1.2	1.6	1.1	1.5
Run 3	90.7	4.4	1.7	0.8	0.9	0.7	0.8
Run 4	89.7	5.0	2.0	0.9	0.9	0.5	1.0
Run 6	92.9	3.4	1.3	0.6	0.6	0.5	0.7
Run 7	90.4	4.5	1.8	0.9	0.9	0.6	0.9

Polymers described in Table 1.

Table 3
Results of the bulk polymerization of propylene with Cat-D at different temperature

Run[a]	Polym. Temp. (°C)	Activity kgPP/gcat	M_W 10^4	MWD	T_m °C
8	30	4.1	36.6	13.0	160.0
9	40	8.0	45.9	12.2	160.2
10	50	23.5	58.4	11.8	161.7
11	60	31.2	74.4	11.9	162.2
7	70	49.2	77.3	10.7	162.4
12	80	53.4	97.4	11.8	165.0
13	30	4.3	33.4	9.0	159.5
14	40	9.2	42.6	8.7	160.0
15	50	19.8	54.0	8.5	161.6
16	60	30.5	62.9	8.3	161.9
6	70	52.1	70.6	7.4	164.5
17	80	48.2	61.4	7.6	161.9

Run 6,13–17 with CHMDMS as external donor, [CHMDMS]/[Et_3Al] = 0.04 (mol/mol).

[a] Run 7–12 without external donor.

we know that the catalyst with diether as internal donor still has high isospecificity even without external donor because of the difficulty of removing diether from solid catalyst with alkylaluminum [7,8], we presume that diol dibenzoate functions similarly as diether in that it is difficult to be removed from the catalyst with alkylaluminum.

On the other hand, we know that ethyl benzoate in Cat-A is so easy to be removed from solid catalyst by alkylaluminum [12] that a lot of external donor is required to maintain high isospecificity, which makes the catalyst decay rapidly [13,14]. The rate-time profiles of propylene polymerization with different [ED]/[$AlEt_3$] ratio using Cat-D are shown in Fig. 3 and it illustrates that the polymerization rate–time profile of Cat-D is slightly different from that of Cat-A. Though the maximum of polymerization rate of Cat-D decreases with increasing [ED]/[$AlEt_3$] ratio, which is explained by the reason that too much external donor can deactivate some active center, the polymerization rate decay becomes slower with increasing external donor, and even when external donor increases to a high degree such as Si/Al = 1, the polymerization rate-time profile type changes from a type that polymerization rate starts at a maximum value followed by a rapid decrease to a type that shows a settling period before reaching a maximum followed by a slow moderate decay rate. These results are different from those of catalyst with ethyl benzoate as internal donor, in the profile of which the polymerization rate decays more rapidly with increasing external donor [13].

Results of the bulk propylene polymerization and main characteristics of the resulting polymers are summarized in Table 3. The activity of the catalyst is influenced by variation of polymerization temperature. The activity of the catalyst increased when the polymerization temperature was raised from 30 to 70 °C whenever with or without external donor. According to Arrhenius formular: $K = A \times \exp(-E_a/RT)$ and the first-order dependence of polymerization rate on propylene concentration [15], one can get the relation between activity and polymerization temperature.

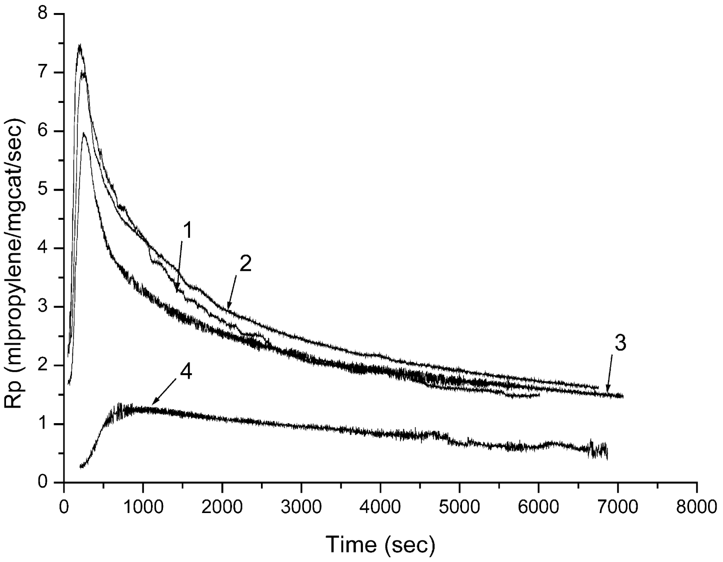


Fig. 3. Rate–time profiles of propylene polymerization with different [CHMDMS]/[$AlEt_3$] ratio slurry polymerization, (1) Si/Al = 0, (2) Si/Al = 0.04, (3) Si/Al = 0.2, (4) Si/Al = 1.

Fig. 4 shows the relation between $\ln(R_p/[M])$ and $1/T$ in bulk polymerization with the catalyst with or without external donor for 1 h, and the apparent activation energy of 57 kJ/mol for polymerization with CHMDMS as external donor or 60 kJ/mol for polymerization without external donor is obtained from 30 to 70 °C, which implies that the external donor does not affect much on propylene polymerization with Cat-D. Fig. 4 also shows that the apparent activation energy of propylene liquid bulk polymerization using Cat-D at temperature higher than 70 °C is different from that of lower than 70 °C no matter with or without external donor, and the phenomena that the apparent activation energy changes with temperature was also found in $MgCl_2$-supported catalyst with other internal donor [16]. It should be noted that the activity, M_w and T_m are highest at 80 °C without external donor, however, all the data were dropped down with external donor, which may imply that the activity and isotacticity of active site coordinated with external donor decrease at temperature over 70 °C, such as 80 °C.

The GPC curves of obtained polymer by Cat-D without external donor are shown in Fig. 5 and it is obvious that all curves are bi-modal. The fraction with higher molecular weight of obtained polymer increases with rising polymerization temperature. Comparatively, it can be also found that the fusion curves of obtained polymers are bi-modal (see Fig. 6). The peak with higher melting temperature become higher comparatively to the peak with lower melting temperature, While the peak with higher melting temperature changes less, the peak with lower melting temperature moves to higher temperature with rising polymerization temperature. As we know that the melting temperature (T_m) is mainly related to the microtacticity of the polymer and high isotacticity means high melting temperatures, and we also know that high isospecificity active center produces polymer with high molecular weight and atactic center produces polymer with lower molecular weight [17]. Kakugo et al. [17–19] divided the active sites into three sites: non-stereospecific site, less isospecific site, and highly isospecific site and we can get the result that there are two highly isospecific sites in Cat-D with AlEt3 system from these division and the result of DSC. The results of GPC and DSC analysis of polymer obtained at different temperature show that the fraction of polymer with higher isotacticity increases, but its melting temperature maintains constant, and the fraction of polymer with lower isotacticity decreases, but its melting temperature increases with polymerization temperature rising, which may be caused by the reason that the activity of higher isospecific site increases but its isospecificity does not change, and the isospecificity of lower isospecific site increases in two highly isospecific sites with temperature rising from 30 to 80 °C. Similar phenomenon is also found in Cat-D with $AlEt_3$ and CHMDMS system (see Figs. 7 and 8). As we mentioned above, the diol dibenzoate is difficult to be removed from the solid catalyst by aluminium and the result is that the active center coordinated with diol dibenzoate plays a main role in high isospecific sites whenever with or without external donor catalyst system, and leads to similar

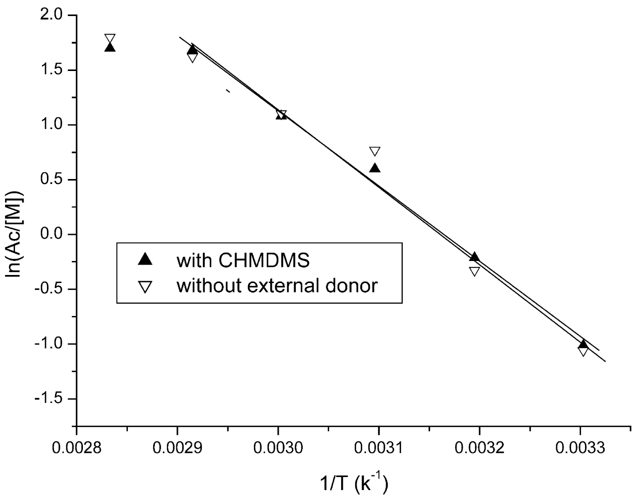


Fig. 4. Relation between $\ln(R_p/[M])$ and $1/T$. Polymerization condition described in Table 3.

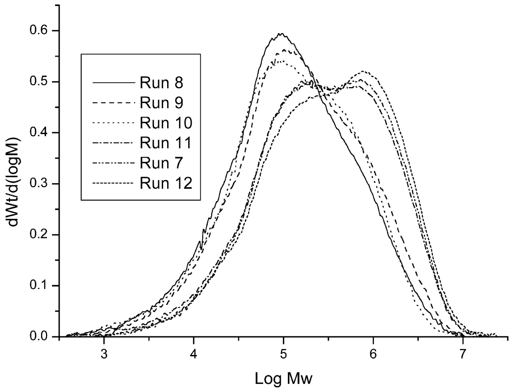


Fig. 5. GPC curves of polymers obtained at different polymerization temperature without external donor. Polymers described in Table 3.

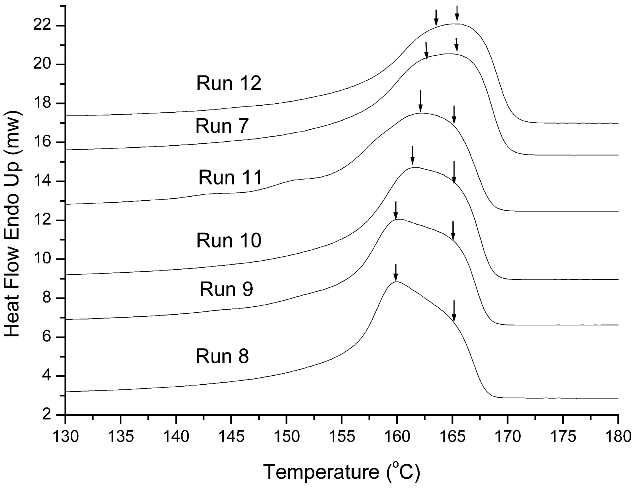


Fig. 6. DSC curves (second fusion) of polymers obtained at different polymerization temperature without external donor. Polymers described in Table 3.

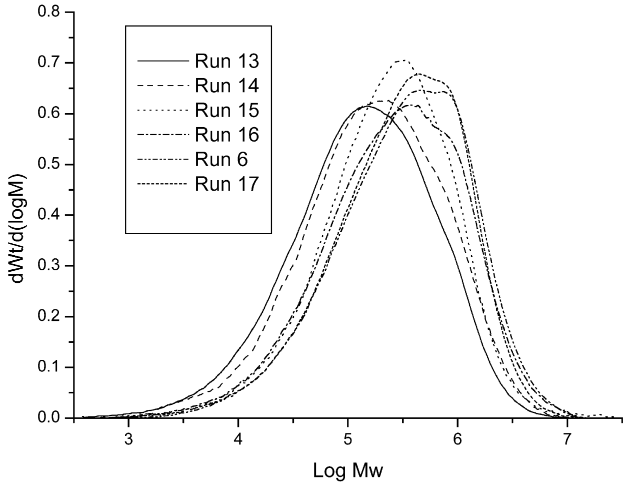


Fig. 7. GPC curves of polymers obtained at different polymerization temperature with CHMDMS as external donor. Polymers described in Table 3.

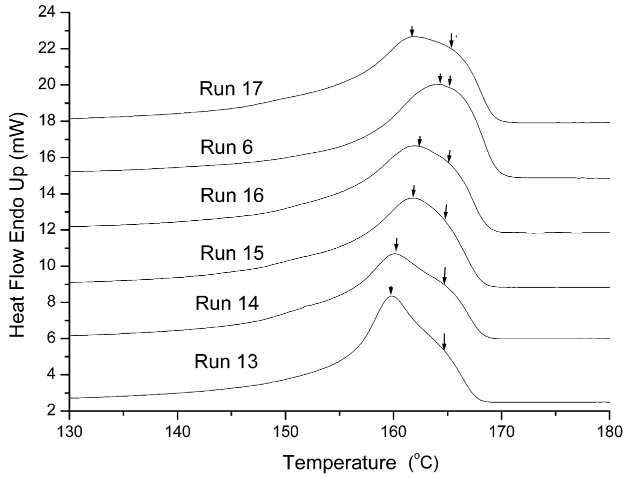


Fig. 8. DSC curves (second fusion) of polymers obtained at different polymerization temperature with CHMDMS as external donor. Polymers described in Table 3.

phenomenon occurred in results of GPC and DSC analysis of polymers obtained by Cat-D with or without external donor.

4. Conclusion

1. The catalyst with 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate as internal donor has high activity and stereo specificity, but poor hydrogen response, and results in relatively wider molecular weight distribution of obtained polymer.
2. The active center coordinated with diol dibenzoate plays a main role in catalyst with 2-isoamyl-2-isopropyl-1,3-propandiol dibenzoate as internal donor with or without external donor system.
3. There are two highly isospecific active sites in catalyst with dibenzoate as internal donor system, the isospecificity of the lower one is strongly affected by polymerization temperature, and the other is less affected.

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