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Journal of Molecular Catalysis A: Chemical 273 (2007) 211–217
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Design of novel malonates as internal donors for $MgCl_2$-supported $TiCl_4$ type polypropylene catalysts and their mechanistic aspects, Part 1

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Received 13 September 2006; received in revised form 25 March 2007; accepted 3 April 2007
Available online 7 April 2007

Abstract

Various new malonate compounds ($R^1R^2C(COOBu)_2$) with different substituents (R^1, R^2) were systematically synthesized and investigated for use as an internal donor (ID) in combination with a $MgCl_2$-supported $TiCl_4$ type catalyst, a triethylaluminum (TEA) co-catalyst and an alkoxysilane external donor (ED) for application in propylene polymerization. The catalytic activity and isotacticity of polypropylene (PP) greatly depended on not only the oxygen electron density of the ED, but also on the molecular volume of the ID. Furthermore, the mechanism of the active site formation was discussed with respect to the composition of the catalyst treated with TEA and ED, and with respect to the temperature rising elution fractionation (TREF) results of PP and so on. It was presumed that the desorption of malonates near Ti species from $MgCl_2$ caused the generation of atactic PP sites, and the decrease of the isotacticity of PP.

Keywords: Computer modeling; Internal donor; Malonate; Poly(propylene) (PP); Ziegler-Natta polymerization

1. Introduction

In industry, polypropylene (PP) is typically manufactured in the presence of the fourth-generation Ziegler-Natta catalyst. The polymerization catalyst is generally prepared from $TiCl_4$ supported by $MgCl_2$, and accompanied with an internal donor (ID), such as di-*n*-butylphthlate (DNBP), a co-catalyst, such as triethylaluminum (TEA), and an external donor (ED), such as dicyclopentyldimethoxysilane (DCPS). The molecular structure and performance of the obtained PP are dominantly controlled by ID and ED [1].

Since the discovery of the phthalate system in 1982, the development of ID has been remarkable, for example 1,3-diethers (e.g. 2,2-diisoamyl-1,3-dimethoxypropane) [2], succinates, such as diisobutyl-2,3-diisopropylsuccinate [3], maleates and malonates [4,5]. It was especially shown that the malonate system had comparatively good activity and high isotacticity [6,7].

A great number of basic studies, particularly in understanding the role of ID (mainly phthalate and 1,3-diether), have been carried out [8–16]. Indeed, a number of outstanding models concerning these active species have been shown by Doi et al., Busico et al., Cavallo and co-workers and Terano [17–20].

Here, although a whole myriad of substituents can be introduced into the second carbon and the ester parts of the malonate structure, the effect of the substitution has not been fully studied. Moreover, the mechanistic aspects of malonate having a different molecular structure from phthalate and 1,3-diether have not been reported at all. Namely, it was expected that basic investigations of malonate systems would be very useful to understand the role of ID and the structures of the active species in not only the malonate system but also in other ID systems. In addition, these investigations are expected to bring an improvement in the PP performance (for example, the replacement of ABS and/or PET resin by new PP having extremely high isotacticity and stiffness). Furthermore, malonate compounds, which are

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doi:10.1016/j.molcata.2007.04.002

neither poisonous nor endocrine disruptors, must be non-toxic and environmentally friendly.

In this paper, computer calculation techniques were used to design new malonate compounds with various substituents, and catalysts formed using these malonates were systematically prepared and evaluated.

2. Experimental part

2.1. Materials

Propylene, hydrogen, TEA, various EDs (except for 1,1-dimethyl-2-methylpropyl-cyclopentyldimethoxysilane: CPTXS) and DNBP were purchased from commercial suppliers and used without further purification. *n*-Heptane was dried over 4A-molecular sieve. CPTXS was synthesized according to reported methods [21].

2.2. Synthesis of malonates

The new malonate compounds used for this work were synthesized by one of two methods. The first method involved the esterification reaction between malonic acids and alcohol, and the second was the alkylation reaction of malonate with NaH and alkyl halide.

The detailed synthetic procedures of malonates, and their corresponding synthetic yields, elemental analyses and ^{1}H NMR spectra are reported here.

2.2.1. Di-n-butyl malonate (BM)

Two hundred grams (1.92 mol) of malonic acid, 1.05 L (11.5 mol) of *n*-BuOH, 770 mL of toluene, and 4 g (0.022 mol) of *p*-toluenesulfonic acid (TsOH) were mixed together in a three-neck flask fitted with a Dean-Stark trap, and stirred under reflux for 4 h until a predetermined quantity of water was produced. Next, after neutralization of the reaction liquid with $NaHCO_3$ (aq), the organic layer was dried with anhydrous Mg_2SO_4, and the remaining toluene was reduced in volume by atmospheric distillation, and further distilled under reduced pressure to give BM. Yield: 380 g (92%), $C_{11}H_{20}O_4$ (216.3): Calcd. C 61.09, H 9.32, O 29.59; Found C 60.20, H 9.00, O 30.80, ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (q, 6H, CH_3, $J = 7.3$ Hz), 1.38 (m, 4H, CH_2CH$_3$), 1.63 (m, 4H, CH$_2$CH_2CH$_2$), 3.36 (d, 2H, O$_2$CCH_2CO$_2$, $J = 7.0$ Hz), 4.14 (q, 4H, CO$_2$CH_2, $J = 6.7$ Hz), b.p.: 75 °C (0.2 mmHg).

2.2.2. Cyclopropane-1,1-di-n-butylcarboxylate (CPBC)

CPBC was synthesized according to the same procedure used to prepare BM, except for using 20 g (0.154 mol) of cyclopropane-1,1-dicarboxylic acid, 84 mL (0.922 mol) of *n*-BuOH, 2 g (0.011 mol) of TsOH and 100 mL of toluene. Yield: 34 g (91%), $C_{13}H_{22}O_4$ (242.3): Calcd. C 64.44, H 9.15, O 26.41; Found C 64.98, H 9.31, O 25.71, ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (t, 6H, CH_3, $J = 7.3$ Hz), 1.40 (m, 4H, CH_2CH$_3$), 1.42 (d, 4H, CH_2 of cyclopropyl, $J = 1.5$ Hz), 1.63 (m, 4H, CH$_2$CH_2CH$_2$), 4.14 (t, 4H, CO$_2$CH_2, $J = 6.7$ Hz).

2.2.3. Cyclobutane-1,1-di-n-butylcarboxylate (CBBC)

CBBC was synthesized according to the same procedure used to prepare BM, except for using 50 g (0.347 mol) of cyclobutane-1,1-dicarboxylic acid, 190 mL (2.08 mol) of *n*-BuOH, 3 g (0.017 mol) of TsOH and 150 mL of toluene. Yield: 77 g (87 %), $C_{14}H_{24}O_4$ (256.3): Calcd. C 65.60, H 9.44, O 24.97; Found C 65.10, H 9.30, O 25.60, ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (t, 6H, CH_3, $J = 7.3$ Hz), 1.37 (m, 4H, CH_2CH$_3$), 1.62 (m, 4H, CH$_2$CH_2CH$_2$), 1.98 (m, 2H, CH$_2$CH_2CH$_2$ of cyclobutyl), 2.54 (m, 4H, CH_2CH$_2$CH_2 of cyclobutyl, $J = 7.9$ Hz), 4.15 (m, 4H, CO$_2$CH_2, $J = 6.7$ Hz).

2.2.4. Di-n-butyl 2,2-dimethylmalonate (BDMM)

BDMM was synthesized according to the same procedure used to prepare BM, except for using 100 g (0.757 mol) of 2,2-dimethylmalonic acid, 415 mL (4.54 mol) of *n*-BuOH, 6 g (0.034 mol) of TsOH and 300 mL of benzene. Yield: 161 g (87%), $C_{13}H_{24}O_4$ (244.3): Calcd. C 63.91, H 9.90, O 26.19; Found C 63.92, H 9.85, O 26.23, ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (t, 6H, CH$_2$CH_3, $J = 7.3$ Hz), 1.36 (m, 4H, CH_2CH$_3$), 1.44 (s, 6H, C(CH_3)$_2$), 1.62 (m, 4H, CH$_2$CH_2CH$_2$), 4.13 (t, 4H, CO$_2$CH_2, $J = 6.7$ Hz), b.p.: 78 °C (0.15 mmHg).

2.2.5. Di-n-butyl 2,2-diethylmalonate (BDEM)

BDEM was synthesized according to the same procedure used to prepare BM, except for using 100 g (0.780 mol) of 2,2-diethylmalonic acid, 428 mL (4.68 mol) of *n*-BuOH, 6 g (0.034 mol) of TsOH and 300 mL of toluene. Yield: 181 g (85 %), $C_{15}H_{28}O_4$ (272.4): Calcd. C 66.14, H 10.36, O 23.50; Found C 66.32, H 10.25, O 23.59.

2.2.6. Di-n-butyl 2,2-di-n-butylmalonate (BDBM)

BDBM was synthesized according to the same procedure used to prepare BM, except for using 100 g (0.543 mol) of 2,2-dibutylmalonic acid, 298 mL (3.26 mol) of *n*-BuOH, 6 g (0.034 mol) of TsOH and 300 mL of toluene. Yield: 152 g (85 %), $C_{19}H_{36}O_4$ (328.5): Calcd. C 69.47, H 11.05, O 19.48; Found C 69.52, H 11.02, O 19.46.

2.2.7. Di-n-butyl 2-methylmalonate (BMM)

Fifteen grams (0.375 mol) of NaH and 450 mL of THF were placed into a three-neck flask under nitrogen atmosphere, and cooled to 0 °C. Seventy-two grams (0.333 mol) of BM was slowly added dropwise to the solution for 1 h, and then agitated for a further 1 h at room temperature to give sodium di-*n*-butyl malonate (first step). Next, 71 g (0.500 mol) of methyl iodide was added slowly to the solution dropwise, and the mixture stirred under reflux for 2 h, to introduce the methyl group (second step). After washing the reaction liquid in NH_4Cl (aq), the organic layer was dried with anhydrous Mg_2SO_4 and the remaining THF reduced by atmospheric distillation, and further distilled under reduced pressure. Yield: 69 g (90%), $C_{12}H_{22}O_4$ (230.3): Calcd. C 62.58, H 9.63, O 27.79; Found C 62.16, H 9.51, O 28.33, ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (m, 6H, CH$_2$CH_3, $J = 7.3$ Hz), 1.38 (m, 4H, CH_2CH$_3$), 1.44 (d, 3H, (O$_2$C)$_2$CHCH_3, $J = 11.0$ Hz), 1.63

(m, 4H, $CH_2CH_2CH_2$), 3.43 (m, 1H, $(O_2C)_2CHCH_3$), 4.13 (m, 4H, CO_2CH_2).

2.2.8. Di-n-butyl 2-cyclopentylmalonate (BCPM)

BCPM was synthesized according to the same procedure used to prepare BMM, except for using 72 g (0.333 mol) of BM, 15 g (0.375 mol) of NaH, 150 g (1.00 mol) of cyclopentyl bromide and 450 mL of THF, where the reaction time of the second step was 16 h. Yield: 81 g (76%), $C_{16}H_{28}O_4$ (284.4): Calcd. C 67.57, H 9.92, O 22.50; Found C 67.70, H 10.00, O 22.30, ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (m, 6H, CH_3, $J = 7.3$ Hz), 1.23 (m, 2H, axial, $(CH_2)_2CH$ of cyclopentyl), 1.38 (m, 4H, CH_2CH_3), 1.58 (m, 4H, $(CH_2)_2(CH_2)_2CH$ of cyclopentyl), 1.62 (m, 4H, $CH_2CH_2CH_2$), 1.85 (m, 2H, equatorial, $(CH_2)_2CH$ of cyclopentyl), 2.48 (m, 1H, $(CH_2)_2CH$ of cyclopentyl), 3.18 (dd, 1H, $CHCH(CO_2)_2$, $J = 10.4$ Hz), 4.12 (m, 4H, CO_2CH_2), b.p.: 86 °C (0.1 mmHg).

2.3. Preparation of solid catalysts

2.3.1. Phthalate catalysts

The $TiCl_4$/DNBP/$MgCl_2$ type catalyst was prepared according to the published method, using $MgCl_2$ as a support material [5]. Also, this catalyst is called DNBP-Cat.

2.3.2. Malonate catalysts

The $TiCl_4$/malonate/$MgCl_2$ type catalysts were prepared using the known method with $Mg(OEt)_2$ as a support material [22]. In addition, these catalysts are called BM-Cat, BMM-Cat, CPCB-Cat, CBCB-Cat, BDMM-Cat, BDEM-Cat, BCPM-Cat and BDBM-Cat, respectively.

2.4. Treatment of solid catalysts

Five grams of the solid catalyst including ID and 50 mL of *n*-heptane were introduced into the 300 mL-reactor, and the slurry was stirred at 40 °C. The solid catalyst was treated by the addition of TEA or TEA/DCPS. After a reaction time, the slurry was immediately filtered and sufficiently washed with heptane. The amounts of ID and ED included in the treated-solid catalysts were determined by GC method.

2.5. Propylene polymerization

The polymerization of propylene was carried out in a stainless steel-autoclave reactor.

2.5.1. Bulk polymerization

Four hundred millilters propylene was introduced into a 1 L-autoclave cooled at 0 °C. After the addition of hydrogen at 1 MPa, the temperature was heated to 70 °C. Next, 20 mL of heptane, 2 mmol of TEA, 0.05 mmol of DCPS and a solid catalyst (0.001 mmol per Ti atom) were introduced into the autoclave, and the bulk polymerization was performed for 60 min. The polymerization was stopped by the addition of 10 mL of MeOH. The obtained polymer was dried for 2 h *in vacuo* at 80 °C [23].

2.5.2. Slurry polymerization

Four hundred millilters of heptane, 2 mmol of TEA and a treated-solid catalyst (0.005 mmol), which was first reacted with TEA or TEA/ED, were introduced into the 1 L-autoclave dried *in vacuo* at room temperature. After the addition of propylene, the temperature was heated to 80 °C and the polymerization was started. After 60 min, the polymerization reaction was quenched by the addition of methanol. The obtained polymer was dried for 2 h *in vacuo* at 80 °C [22].

2.6. TREF measurements

Three milligrams of PP dissolved in *o*-dichlorobenzene (ODCB) as a solvent was loaded to the apparatus equipped with a 4.2 Φ × 150 mm-column filled with Cromosolb-PAW® and an IR-detector. The solution was cooled from 135 to 0 °C at a constant rate (5 °C/h), and the temperature was kept at 0 °C for 10 min to induce crystallization of PP. Next, the temperature was elevated from 0 to 135 °C at 40 °C/h and ODCB as a dissolution reagent of crystallized PP (flow rate: 1.0 mL/min) was fed into the column.

3. Results and discussion

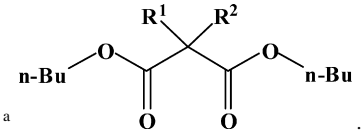
3.1. Effect of malonate substituents as an internal donor

Various new malonate compounds ($R^1R^2C(COOBu)_2$) having different substituents (R^1 and R^2) were synthesized, and the results of the polymerization of propylene using these catalysts (including these malonates as ID) are shown in Table 1. Sadashima et al. had already found a good correlation between the ^{29}Si NMR chemical shift of the various organic alkoxysilane compounds as ED and the electron density of oxygen calculated by the MNDO method. The authors had also shown that the electron density of oxygen in ED had been an important factor for controlling the isotacticity of the obtained PP [21]. Therefore, the molecular volume, the electron density of the carbonyl oxygen, and the distance between the two oxygens of the IDs, were calculated using the MNDO method (semi-empirical method, calculated with MOPAC 93®) [24–26]. Fig. 1(A and B) shows that there was good correlation among the isotacticity of the obtained PP, the catalytic activity and the molecular volume of the malonates. The catalyst including a malonate having an appropriate molecular volume (240–300 Å^3), such as CPBC, BDMB, CBBC, BDEM and BCPM, showed high isotacticity and high activity.

As can be seen from Table 1, the electron density of the oxygen in the malonates was approximately −0.34 a.u., which was close to that of DNBP. The distance between the oxygen atoms of the malonates except for CBBC was in the range of 3.5–3.9 Å, which was similar to that of DNBP. Therefore, it can be presumed that one of the main factors in determining the performance in this system is the molecular volume of the malonate. Indeed, it is considered that not only the ease of approaching $MgCl_2$ is significant for enhancement of the performance, but also the structure after absorbing $MgCl_2$ may be important.

Table 1
Polymerization results with various kinds of IDs

ID[a]			Calculation values of ID[b]			Polymerization[c]	
Name	R^1	R^2	Mole. vol.[d] (Å^3)	O electron charge[e] (a.u.)	O–O distance[f] (Å)	[mmmm][g] (mol%)	Activity (kg/g Cat.)
DNBP	–	–	277	-0.33_7	3.7_6	97.7	27.2
BM	H	H	221	-0.34_3	3.5_3	92.1	0.3
BMM	Me	H	239	-0.34_2	3.7_0	96.9	5.2
CPBC	Cy-Pr		245	-0.34_2	3.7_6	97.6	12.0
BDMB	Me	Me	252	-0.34_8	3.7_9	97.6	16.4
CBBC	Cy-Bu		260	-0.34_4	4.6_5	97.6	15.2
BDEM	Et	Et	285	-0.34_8	3.6_4	97.4	19.5
BCPM	Cy-Pe	H	292	-0.34_4	3.8_6	97.5	24.8
BDBM	*n*-Bu	*n*-Bu	352	-0.34_8	3.6_4	97.0	8.0

[a] 

[b] Calculated by MNDO.
[c] Bulk polymerization (see Section 2).
[d] Van der Waals molecular volume.
[e] Average value of two oxygen atoms of carbonyl groups.
[f] Distance between two oxygen atoms of carbonyl groups.
[g] Determined by ^{13}C NMR.

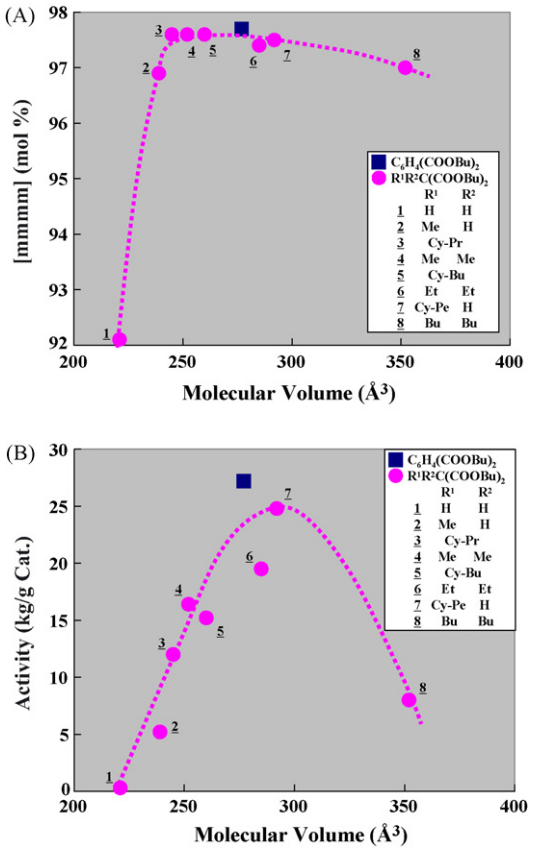


Fig. 1. Relationship between molecular volume of ID and catalysis performance: (A) isotacticity of obtained PP; (B) catalytic activity. Bulk polymerization (see Section 2).

3.2. Effect of alkoxysilane substituents as an external donor

Table 2 shows the comparison results of the polymerization evaluations of DNBP-Cat and BCPM-Cat, which indicated the relatively high isotacticity and activity in Table 1, using various organic alkoxysilane compounds ($R^1R^2Si(OMe)_2$) having different substituents (R^1 and R^2) as ED. The molecular volume, the electron density of oxygen, and the distance between the two oxygen atoms of the EDs were calculated by MNDO. The relationship among the electron density of oxygen in the EDs, the isotacticity of PP, and the catalytic activity, are shown in Fig. 2(A and B), respectively.

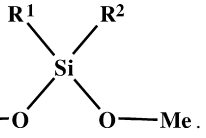
Consequently, as shown in Fig. 2, using an ED having a large oxygen electron density, the isotacticities and activities of both catalyst systems were increased (the distance between the oxygen atoms was almost constant at 2.6–2.7 Å, as shown in Table 2. It seems that the molecular volume mainly contributes to the molecular-weight-distribution control [21].). Furthermore, when the same ED was used, the BCPM system indicated a lower isotacticity than the DNBP system by 2 mol%, but when DCPS was used as an ED, the difference in isotacticity between the two systems was reduced to 0.2 mol%. Moreover, the activities of both catalyst systems were almost equal, and the maximum values were obtained by the use of DCPS.

3.3. Mechanism of the active site formation

In order to clarify the role of the donor, and the mechanism of the active site formation in the BCPM catalyst system, BCPM and DNBP having various donor compositions were prepared, and the resulting TREF data of PP obtained by polymerization using these catalysts, together with their compositions, were tabulated in Table 3. Here, the conditions of catalyst treatment and polymerization were described in the footnotes of Table 3 and

Table 2
Effect of combination with ID and ED on polymerization performance

ID	ED[a]			Calculation values of ED[b]			Polymerization[c]		
	Name	R^1	R^2	Mole. vol.[d] (Å^3)	O electron charge[e] (a.u.)	O–O distance[f] (Å)	[mmmm][g] (mol%)	Activity (kg/g Cat.)	M_w/M_n
DNBP	DMS	Me	Me	125	-0.67_3	2.6_4	83.4	6.8	–
↓	CHMS	Cy-Hx	Me	199	-0.68_0	2.6_2	95.9	18.4	4.2
↓	IPIBS	i-Pr	i-Bu	210	-0.68_5	2.6_1	97.3	20.1	4.7
↓	CHIBS	Cy-Hx	i-Bu	250	-0.68_6	2.6_1	97.7	21.2	–
↓	CPIBS	Cy-Pe	i-Bu	233	-0.68_8	2.6_3	97.7	23.5	–
↓	DCPS	Cy-Pe	Cy-Pe	240	-0.69_0	2.6_3	97.7	27.2	5.4
↓	DTBS	*t*-Bu	*t*-Bu	226	-0.71_8	2.6_8	97.7	19.2	5.4
↓	CPTXS	Cy-Pe	Thexyl	267	-0.70_8	2.6_8	97.7	18.0	6.7
BCPM	DMS	Me	Me	125	-0.67_3	2.6_4	78.3	8.0	–
↓	CHMS	Cy-Hx	Me	199	-0.68_0	2.6_2	94.2	16.8	3.9
↓	IPIBS	i-Pr	i-Bu	210	-0.68_5	2.6_1	95.1	19.6	–
↓	CHIBS	Cy-Hx	i-Bu	250	-0.68_6	2.6_1	95.6	21.6	–
↓	CPIBS	Cy-Pe	i-Bu	233	-0.68_8	2.6_3	95.7	23.2	5.2
↓	DCPS	Cy-Pe	Cy-Pe	240	-0.69_0	2.6_3	97.5	24.8	–
↓	DTBS	*t*-Bu	*t*-Bu	226	-0.71_8	2.6_8	95.7	21.2	–



[a] .
[b] Calculated by MNDO.
[c] Bulk polymerization (see Section 2).
[d] Van der Waals molecular volume.
[e] Average value of two oxygen atoms.
[f] Distance between two oxygen atoms.
[g] Determined by ^{13}C NMR.

Table 3
Effect of ID and ED on TREF curves of obtained polymer

Run[a] number	ID	Catalyst composition[b]		ED/Ti molar ratio[c]	TREF pattern[d]		
		ID (mmol/g Cat.)	ED (mmol/g Cat.)		APP[e] (wt%)	Middle[f]-IPP (wt%)	Peak[g] (°C)
1	DNBP	0.344	0	50/1	0.97	22.7	117.0
2	↓	0.071	0	0/1	42.6	55.8	111.6
3	↓	0.059	0.091	0/1	3.97	39.1	117.7
4	↓	0.044	0.172	0/1	2.64	41.1	117.0
5	↓	0.038	0.189	0/1	2.36	31.9	118.0
6	↓	0.036	0.184	0/1	2.40	30.3	118.2
7	↓	0.033	0.200	0/1	2.70	28.4	116.9
8	BCDM	0.517	0	50/1	2.56	40.5	117.3
9	↓	0.082	0	0/1	32.7	66.0	111.7
10	↓	0.049	0.099	0/1	6.25	53.8	116.4
11	↓	0.034	0.179	0/1	5.61	42.2	117.0
12	↓	0.041	0.193	0/1	5.25	45.7	116.7
13	↓	0.020	0.190	0/1	6.65	43.9	117.0
14	↓	0.003	0.193	0/1	6.83	43.6	116.4

[a] Catalyst treatment: run no. 1 and 8: none; run no. 2 and 9: TEA, Al/Ti (molar ratio) = 4/1, temperature: 40 °C, time: 120 min; run no. 3–7 and 10–14: TEA, DCPS, Al/Si/Ti (molar ratio) = 4/2/1, temperature: 40 °C, time: 1–120 min. Polymerization (see Section 2): run no. 1 and 8: TEA/DCPS; run no. 2–7 and 9–14: TEA.
[b] Determined by GC (see Section 2).
[c] Polymerization condition (see Section 2).
[d] TREF measurement (see Section 2).
[e] The amounts of 0 °C soluble parts.
[f] The amounts of middle elution temperature fraction (20–115 °C).
[g] Peak temperature of high elution temperature fractions (115–135 °C).

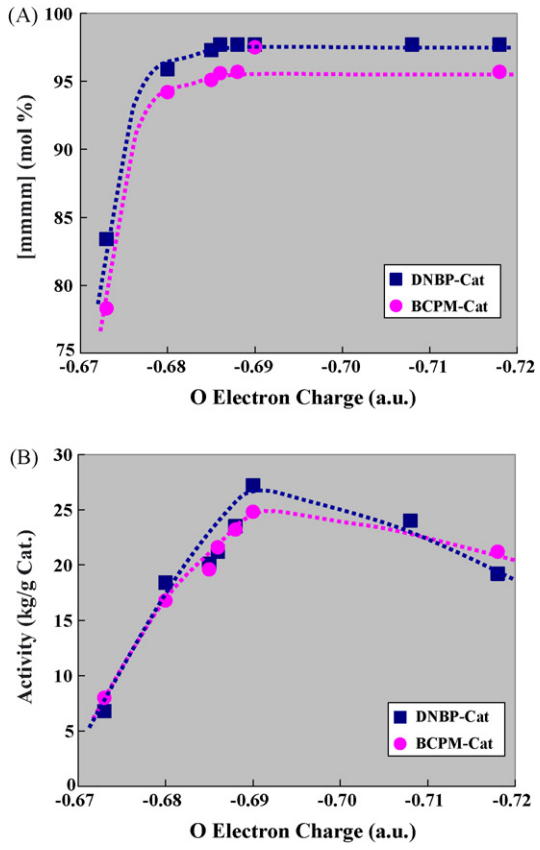


Fig. 2. Relationship between O electron charge of ED and catalysis performance: (A) isotacticity of obtained PP; (B) catalytic activity. Bulk polymerization (see Section 2).

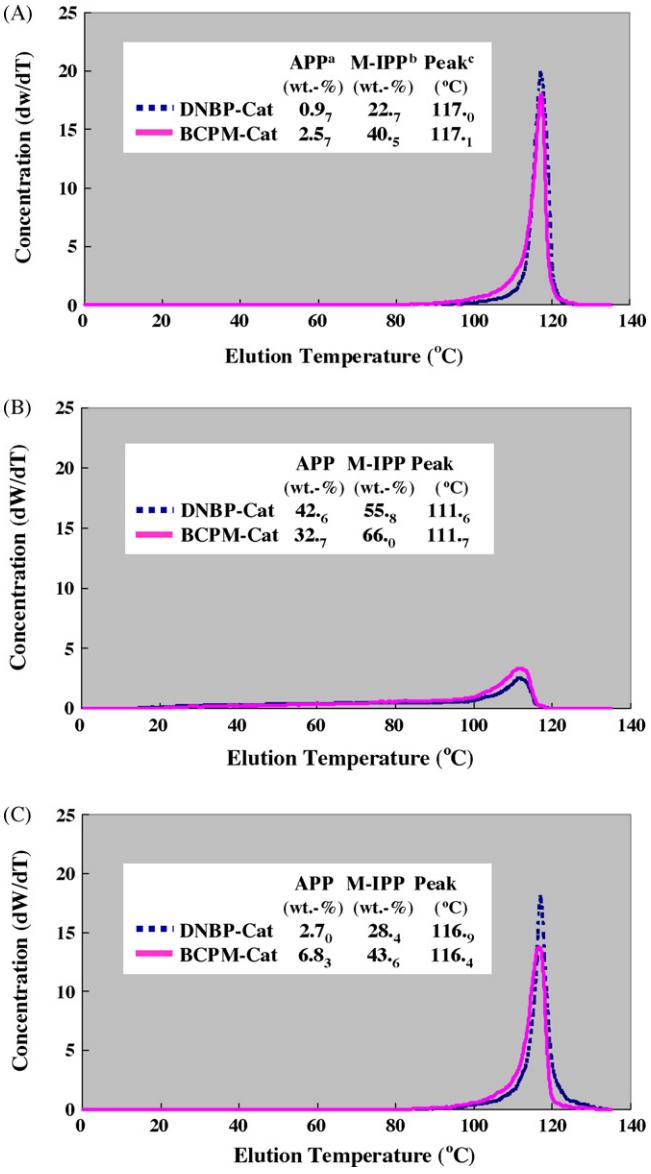


Fig. 3. Comparison of TREF curves obtained from different catalyst systems. [a]Peak temperature of high elution temperature fractions (115–135 °C). [b]The amount of 0 °C soluble parts. Catalyst treatment: (A) none (runs 1 and 8 in Table 3); (B) TEA, Al/Ti (molar ratio) = 4/1, temperature: 40 °C, time: 120 min (runs 2 and 9 in Table 3); (C) TEA, DCPS, Al/Si/Ti (molar ratio) = 4/2/1, temperature: 40 °C, time: 120 min (runs 7 and 14 in Table 3). Polymerization (see Section 2): (A) TEA/DCPS; (B and C) TEA.

in Section 2. It was expected that only the ID affected the formation of the active species for runs 2 and 9, but both ID and ED contributed to the active species formation for the remaining runs. Moreover, the typical TREF charts (runs 1, 2, 7, 8, 9 and 14) are shown in Fig. 3. Furthermore, the change of donor composition in the course of treatment using TEA/ED (runs 3–7 and 10–14) and the values of the corresponding TREF data are indicated in Fig. 4.

As shown in runs 1, 8 and in Fig. 3(A), the peak temperature of the main fraction of PP obtained by the two catalyst systems was equal at 117 °C, whereas compared to the existing DNBP system, the width of the main peak in the BCPM system was broadened to the slightly lower temperature side, and the amount of soluble parts at 0 °C (APP) was larger than that of the BCPM system. Consequently, this seems to reflect the results of the slightly lower isotacticity of PP obtained with the BCPM system rather than with the DNBP system (97.5 < 97.7 mol%, Δ[mmmm]: 0.2 mol% as shown in Tables 1 and 2).

Although there was a large amount of APP and the middle elution temperature fraction (20–115 °C) in runs 2, 9 and in Fig. 3(B) on which ED was of no effect, the APP decreased and the high elution temperature fraction (115–135 °C) increased in runs 1, 8 and in Fig. 3(A), and runs 3–7, 10–14 and in Fig. 3(C), on which ED was of effect in the polymerization or treatment step in both catalyst systems. Therefore, it turns out that ED has also an important role in improving the isotacticity in the malonate system.

In runs 3–7, 10–14 and in Fig. 4(A), the peak temperature of the high elution temperature fraction of both catalyst systems was almost the same (near 117 °C). Moreover, in runs 1, 3–7, 8, 10–14 and in Fig. 4(C), the tendency for ID to be extracted by TEA and exchanged with ED in advance of the reaction was well agreed in both systems. Hence, it was expected that this process was essentially similar to the formation of the high-IPP site. In runs 1, 3–7, 8, 10–14 and in Fig. 4(B), the amount of APP became fixed after a gradual reduction in the DNBP system. On the other hand, after reduction for about 20 min, the amount of

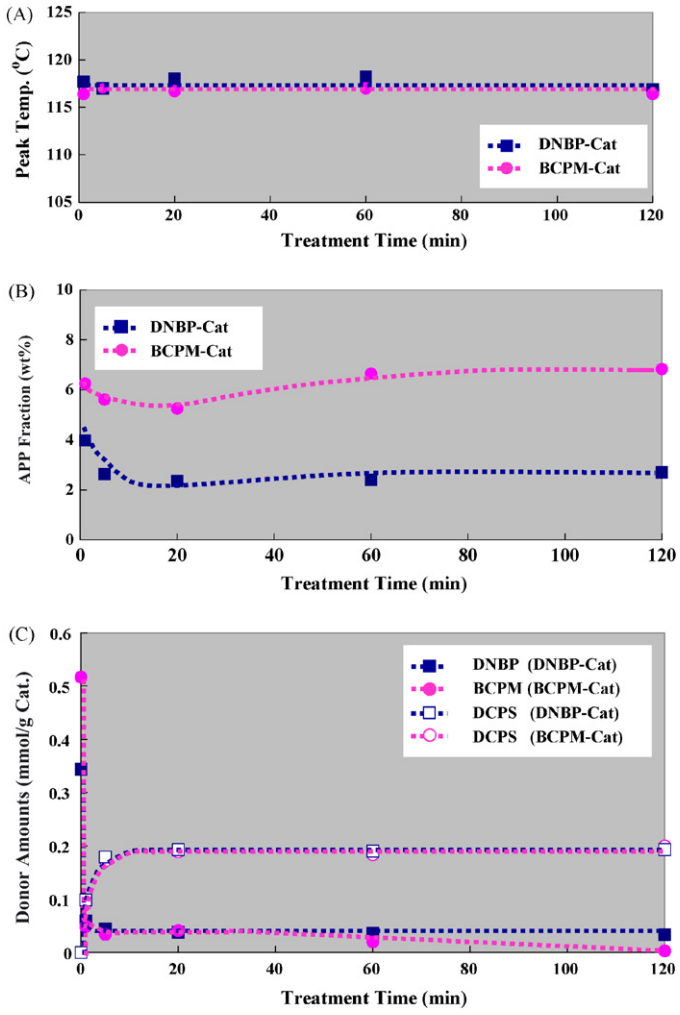


Fig. 4. Relationship between donor compositions and TREF patterns of PP polymers obtained with treated catalysts. Catalyst treatment: TEA, DCPS, Al/Si/Ti (molar ratio) = 4/2/1, temperature: 40 °C, time: 1–120 min (runs 3–7 and 10–14 in Table 3). Polymerization (see Section 2): TEA.

APP increased and became fixed in the BCPM system. Furthermore, in runs 1, 3–7, 8, 10–14 and in Fig. 4(C), while DNBP remained in the catalyst until the end of the reaction, BCPM was completely extracted during the reaction. Therefore, the formation of APP sites in both systems clearly differed from each other, and it was considered that the behavior of malonate mentioned above caused an increase in the amount of APP obtained by the malonate system.

4. Conclusion

Propylene (PP) polymerization using $TiCl_4$/malonate/$MgCl_2$ type catalysts with the newly synthesized malonate compounds ($R^1R^2C(COOBu)_2$) having various substituents as internal donors (IDs) was investigated. The catalysts having a malonate with an appropriate molecular volume indicated high isotacticity and high activity.

Moreover, it was suggested that the malonate system formed high-IPP active species through the donor exchange of ID and ED, which was similar to the existing phthalate system.

On the other hand, the malonate system produced a relatively large amount of APP and middle-IPP. One of the main causes for the likely formation of the APP site was the desorption of malonates near the Ti species.

We will report further investigations considering the selective adsorption nature of ID with respect to the specific faces of $MgCl_2$.

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