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Feature Article

PRECISE SYNTHESIS OF OLEFIN BLOCK COPOLYMERS USING A SYNDIOSPECIFIC LIVING POLYMERIZATION SYSTEM

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Abstract This feature article summarizes the synthesis of novel olefin block copolymers using fast syndiospecific living homo- and copolymerization of propylene, higher 1-alkene, and norbornene with *ansa*-fluorenylamidodimethyltitanium-based catalyst according to the authors' recent results. The catalytic synthesis of monodisperse polyolefin and olefin block copolymer was also described using this living system.

Keywords: Single-site catalyst; Propylene; Norbornene; Living polymerization; Block copolymer.

INTRODUCTION

Since the discover of the group 4 metallocene catalysts by Kaminsky and co-workers[1], the development of well-defined homogeneous Ziegler-Natta catalysts, *i.e.*, so-called single-site catalysts has offered a detailed understanding of the mechanism and stereochemistry of olefin polymerization to give a variety of olefin-based homo- and copolymers with precise control of the first-order structure[2–5].

One of the new areas developed by the single-site catalysts is living polymerization of olefins, in which neither chain transfer nor deactivation occurs. Living polymerization is not only useful for the synthesis of block copolymers with predictable molecular weights and narrow molecular weight distributions (MWDs) but also applicable to investigate the nature of active centers due to its simple kinetics. Since the first living polymerization of propylene was reported with the V-based homogeneous catalyst in the end of 1970s[6], much effort has been paid for living polymerization of olefins by designing the structure of complexes and controlling the polymerization conditions[7, 8].

We have previously reported that [*t*-BuNSiMe_2Flu]TiMe_2 (**1**) combined with Me_3Al-free dried MAO (dMAO) or dried modified MAO (dMMAO) conducted highly active syndiospecific living polymerization of propylene at 0°C[9, 10]. The introduction of the *t*Bu groups on the fluorenyl ligand of **1** at 3,6-position ([*t*-BuNSiMe_2(3,6-*t*Bu_2Flu)]TiMe_2 (**2**)), 2,7-position ([*t*-BuNSiMe_2(2,7-tBu_2Flu)]TiMe_2 (**3**)), and 2,3,6,7-position ([*t*-BuNSiMe_2($C_{29}H_{36}$)]TiMe_2 (**4**)), enhanced the activity and the syndiospecificity with keeping the living manner. The activity (kg-polymer mol-Ti^{-1} h^{-1}) and syndiospecificity (rr) obtained with **1**, **2**, **3**, and **4** using dMMAO as a cocatalyst were as follows: **1**, 660, 73%; **2**, 2320, 93%; **3**, 2280, 81%; **4**, 11400, 61%[11, 12]. These

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catalytic systems are also useful for the syndiospecific living polymerization of higher 1-alkenes[13]. This article introduces the synthesis of block copolymers composed of propylene and/or norbornene monomer using highly syndiospecific living polymerization system of **2**-dMMAO. We also succeeded in catalytic synthesis of monodisperse polypropylene (PP) and block copolymer with this living system.

LIVING RANDOM COPOLYMERIZATION

Copolymerization of norbornene and propylene with **2** activated by dMMAO was performed in toluene at 20°C under an atmospheric pressure of propylene by changing polymerization time. The results are summarized in Table 1.

Table 1. Copolymerization of norbornene (NB) with propylene and 1-octene[a]

Entry	Comonomer	Time (min)	Yield (g)	$M_n{}^b \times 10^{-4}$	MWD [b]	NB in copolymer [c] (mol%)	$T_g{}^d$ (°C)
1	Propylene	1.0	0.12	2.1	1.21	–[e]	247
2	Propylene	2.0	0.25	4.3	1.13	–[e]	245
3	Propylene	3.0	0.39	6.4	1.11	–[e]	248
4	Propylene	4.0	0.53	8.2	1.12	78	252
5	1-Octene	1.5	0.40	4.9	1.15	82	233

[a] Polymerization conditions: Ti, 10 μmol, Al, 2.0 mmol; propylene: 101.3 kPa, NB, 0.9 mol/L; [b] Number average molecular weight and molecular weight distribution determined by GPC using universal calibration; [c] Determined by ^{13}C-NMR; [d] Determined by DSC; [e] Not determined

The catalytic system showed high activity and gave high molecular-weight (M_n) with narrow molecular-weight distribution (MWD) (entry 1, Table 1). The yield and M_n value were increased according to the polymerization time, and the yield and M_n showed a good linear relationship (Fig. 1a). The GPC curves of the copolymers shifted to the higher molecular weight region with keeping narrow MWDs (Fig. 1b). The results testified that the copolymerization of propylene and norbornene proceeded in a living manner.

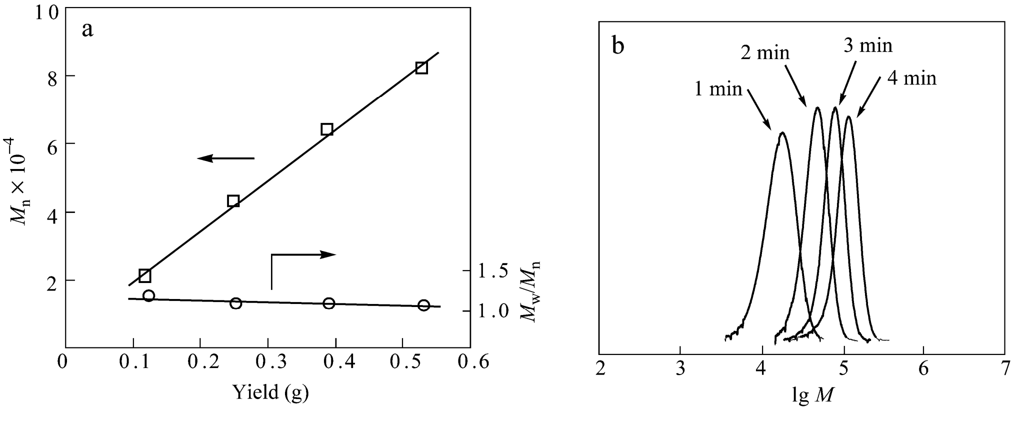


Fig. 1 Plots of M_n and MWD values against yield (a) and GPC curves (b) of propylene-norbornene copolymers obtained with **2**-dMMAO (Reproduced with permission from the literature [14])

^{13}C-NMR spectrum of norbornene-propylene copolymer (entry 4, Table 1) indicates the production of random copolymer, and the norbornene content was determined to be 78 mol%. The thermal properties of the copolymers were then investigated by DSC, and the results are shown in Table 1. The DSC results indicate that all the copolymers were amorphous with high T_g values near 250 °C[14].

Copolymerization of norbornene and 1-octene (entry 5, Table1) also showed the same phenomenon with the copolymerization of norbornene and propylene, which testified that living random copolymerization of norbornene and higher 1-octene also proceeded with high activity[15, 16].

SYNTHESIS OF OLEFIN BLOCK COPOLYMERS

Synthesis of Stereoblock PP

The effects of monomer concentration in syndiospecific living polymerization of propylene with **2**-dMMAO were investigated. Table 2 summarizes the results of propylene polymerizations under various pressure of propylene in heptane at 0 °C. The catalytic system showed high activity and gave high M_n PP for 4 min under an atmospheric pressure. According to the decrease of the propylene pressure, the activity was decreased, and the numbers of polymer chains (N) were smaller than that of the Ti used with keeping the narrow MWD, which suggested that the propylene polymerization proceeded in a living manner regardless of the propylene pressure.

Table 2. Propylene polymerization with **2**-dMMAO under various pressure of propylene [a]

Entry	Pressure [b] (kPa)	Time (min)	Yield (g)	Activity [c]	M_n [d] $\times 10^{-4}$	MWD [d]	N [e] (μmol)	rrrr [f] (%)	T_m [g] (°C)
6	101.3	4	1.96	1470	11.1	1.35	18	0.83	125
7	81.0	6	2.16	1080	12.1	1.33	17	0.68	106
8	60.8	8	2.56	960	13.9	1.28	18	0.56	88
9	40.5	10	2.09	627	12.1	1.27	17	0.45	73
10	20.3	10	1.23	369	9.1	1.22	14	0.42	–[h]
11	10.1	10	0.47	141	3.7	1.31	13	0.39	–[h]

[a] Polymerization conditions: Ti, 20 μmol, Al, 4.0 mmol; [b] Propylene pressure + vapor pressure of heptane (1.52 kPa) at 0 °C; [c] Activity in kg-PP/(mol-Ti·h); [d] Number average molecular weight and molecular weight distribution determined by GPC using universal calibration; [e] Calculated from yield and M_n; [f] Determined by ^{13}C-NMR spectroscopy; [g] Determined by DSC; [h] Not detected

The catalyst system gave highly syndiotactic crystalline PP under 101.3 kPa with the rrrr value of 0.83 and the T_m of 125 °C (entry 6, Table 2). The rrrr values of the PPs obtained were decreased with lowering the propylene pressure accompanied by decrease in the T_m of the PPs. As a consequence, amorphous polymers were obtained under 20.3 and 10.1 kPa (entries 10 and 11, Table 2). The low syndiospecificity under lower propylene concentration is ascribed to the promotion of the "chain migration" but not to the low selectivity of the prochiral face at the enantiomorphic site[17].

We therefore tried to synthesize syndiotactic-atactic stereoblock PP by changing the propylene pressure. The polymerization results and the GPC curves of the polymers are shown in Fig. 2. The yields and M_n values

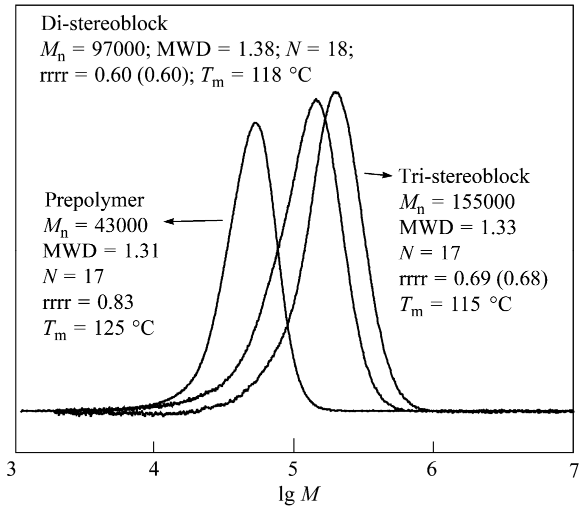


Fig. 2 Polymerization results and GPC curves of the PPs obtained by changing propylene pressure during living polymerization (Reproduced with permission from the literature [18])

were increased compared with those of the first- and second-step polymers respectively with keeping the constant *N* value and narrow MWD, and any other peaks or shoulders were not observed in the GPC curves of the second and third step.

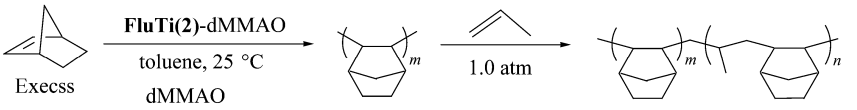
The calculated rrrr values are also shown in parentheses of Fig. 2, which were calculated from the weight fraction of each block sequence assuming that the pentad distributions of each block sequence are the same as those of the PPs obtained under 20.3 and 101.3 kPa, respectively. The observed values are in good accordance with the calculated values both in the second- and third-step PPs. The second-and third-step PPs showed T_m of 118 °C and 115 °C. These results indicate the formation of the expected syndiotactic-atactic and syndiotactic-atactic-syndiotactic stereoblock living PPs by changing propylene pressure[18].

The syndiospecificity of this catalytic system depends not only on the propylene pressure but also on the polymerization solvent and temperature. Therefore, di-stereoblock PPs were also synthesized by the addition of polar solvent[19] or by changing polymerization temperature during living polymerization[20].

Synthesis of Propylene- and Norbornene-based Block Copolymers

The synthesis of polynorbornene-*block*-poly(propylene-*ran*-norbornene) (PNB-*b*-P(P-*ran*-NB) was conducted as follows: after homopolymerization of norbornene for a short period, an atmospheric pressure of propylene was introduced, and copolymerization was conducted with the remained norbornene for a few minutes. The propylene concentration was kept constant under atmospheric pressure of propylene, and the comonomer composition was controlled by the initial concentration of norbornene. The results of the block copolymerization are summarized in Table 3.

Table 3. Synthesis of PNB-*b*-P(P-*ran*-NB) with **2**-dMMAO [a]



Entry	Monomer (g)	Time (min)	Yield (g)	Product	M_n [b] × 10^{-4}	M_w/M_n [b]	T_g (°C) [d]
12	NB (4.5)	1.5	1.47	PNB	11.3	1.09	–
13	NB (4.5) + P[c]	1.5 + 2	3.30	PNB-*b*-P(P-*ran*-NB)	25.8	1.19	240
14	NB (1.2)	1	0.73	PNB	6.2	1.07	–
15	NB (1.2) + P[c]	1 + 1	1.07	PNB-*b*-P(P-*ran*-NB)	9.2	1.19	191

[a] Conditions: Ti, 20 μmol, Al, 4.0 mmol; [b] Determined by GPC using polystyrene standards; [c] During the norbornene polymerization, an atmospheric pressure of propylene was added and copolymerization was conducted for a few minutes; [d] Determined by DSC

Homopolymerization of norbornene showed high activity of approximately 3 ton-polymer/(mol-$Ti^{-1}\cdot h^{-1}$) and gave PNBs with extremely narrow MWD, which suggested that the catalytic system should conduct living polymerization of norbornene (entries 12 and 14, Table 3). After the copolymerization, the yields were increased accompanied by the increase of M_n values with keeping the narrow MWDs, regardless of the comonomer composition (entries 13 and 15, Table 3). The GPC curves of second step shifted to higher molecular weight region compared with those of first step, and no peak or shoulders were observed in any other area.

The ^{13}C-NMR spectra of the PNB (entry 12, Table 3) and the block copolymer (entry 13, Table 3) are shown in Fig. 3, where the resonances of the random sequences of propylene and norbornene are observed. The block copolymers showed T_g which corresponds to the amorphous P(P-*ran*-NB) sequence. The T_g values (191–240 °C) were controlled by the comonomer composition, which is in good agreement with that obtained with the nonsubstituted original complex **1**[21]. These results also testified the formation of PNB-*b*-P(P-*ran*-NB)[22].

The synthetic results of syndiotactic PP-*b*-P(P-*ran*-NB) are summarized in Table 4. To increase the syndioregularity of syndiotactic PP, the author conducted propylene polymerization in toluene at −20 °C under atmospheric pressure of propylene. After the 5 min homopolymerization, a prescribed amount of norbornene was added and copolymerization was conducted for 6 min with raising the polymerization temperature to 25 °C. The PP obtained in the first step had the M_n value of 108000 with MWD of 1.36 and showed the T_m at 135 °C (entry 16, Table 4). After the copolymerization, the yields were increased accompanied by the increase of M_n values (208000–226000) and the decrease of MWD values (1.21–1.32) regardless of the amount of norbornene added (entries 17–19). All the GPC curves of second step shifted to higher molecular weight region compared with those of first step, and no peak or shoulders were observed in the other area.

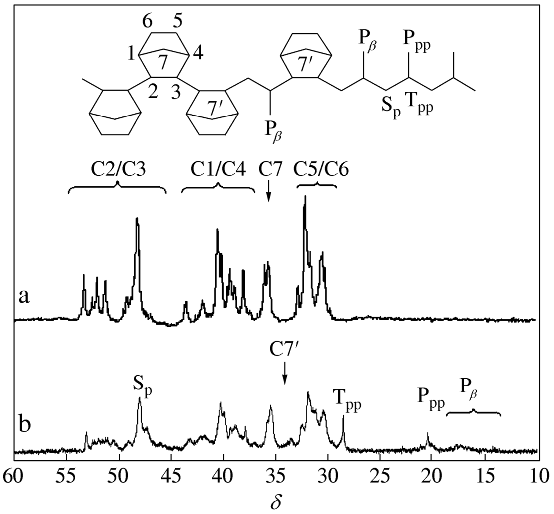
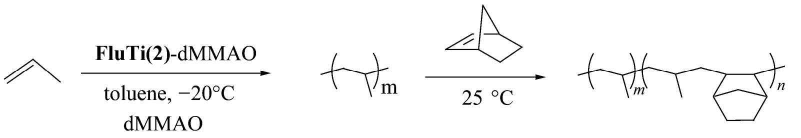


Fig. 3 ^{13}C-NMR spectra of PNB (a, entry 12) and P(P-*ran*-NB) (b, entry 13)

Table 4. Synthesis of PP-*b*-P(P-*ran*-NB) with 2-dMMAO [a]



Entry	*N* (g)	Time (min)	Yield (g)	M_n [b] × 10^{-4}	M_w/M_n [b]	T_m (°C) [c]	T_g (°C) [c]
16 (prepolymer)[d]	0	0	0.48	10.8	1.36	135	–
17	2.77	6	0.92	20.8	1.21	135	311
18	2.07	6	1.12	22.4	1.30	133	231
19	1.38	6	1.09	22.6	1.32	133	93

[a] Conditions: Ti, 10 μmol, Al, 2.0 mmol; [b] Determined by GPC using polystyrene standards; [c] Determined by DSC; [d] Propylene: 101.3 kPa, time: 5 min

The ^{13}C-NMR spectrum of the block copolymer (entry 17) is shown in Fig. 4. The resonances of the random sequences of propylene and norbornene were observed together with those of syndiotactic PP sequences in the spectrum of the block copolymer.

The DSC results indicate that the copolymers showed both T_m (133–135 °C) and T_g that correspond to the crystalline syndiotactic PP sequence and amorphous P(P-*ran*-NB) sequence, respectively. The T_g values were controlled by the amount of norbornene added (93–311 °C), which is in good agreement with that obtained with the nonsubstituted original complex **1**, where the T_g values of copolymers can be controlled widely (53–249 °C) by changing the propylene/norbornene feed ratio[21]. These results also testified the formation of the expected block copolymers, *i.e.*, syndiotactic PP-*b*-P(P-*ran*-NB).

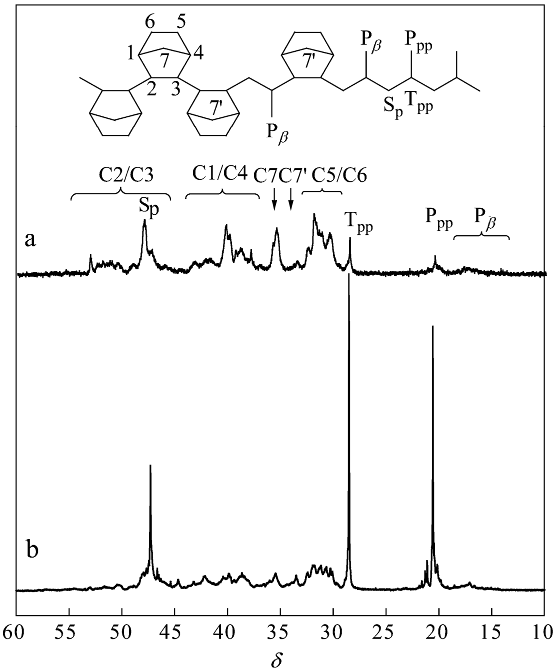


Fig. 4 ^{13}C-NMR spectra of P(P-*ran*-NB) (a) and PP-*b*-P(P-*ran*-NB) (b, entry 17)

CATALYTIC SYNTHESIS OF MONODISPERSE OLEFINS

As described above, living polymerization is a useful method for the synthesis of polymers with precisely controlled structures such as monodisperse polymers, terminally functional polymers and block copolymers. Living polymerization is however not an efficient method of polymer production, because one initiator produces only one polymer chain.

On the contrary, monodisperse polymer should be obtained even in the presence of a chain transfer reagent if the propagation rate is much faster than that of the chain transfer or chain transfer occurs only after all the monomer has been consumed. In this case, monodisperse polymers can be catalytically obtained by the successive addition of the same amount of monomer at a certain interval. The Mitsui group actually reported the catalytic production of monodisperse Zn-terminated polyethylenes with a bis(phenoxy-imine)titanium dichloride activated by methylaluminoxane, where 80 equivalents of $ZnEt_2$ was added after the first-polymerization and the second-polymerization was conducted in the presence of $ZnEt_2$[23].

If we select an adequate chain transfer reagent with a suitable amount, we could obtain monodisperse polypropylene catalytically using this living system. From this view point, we reinvestigated propylene polymerization with **1**-MMAO and found that the presence of a suitable amount of TIBA produced monodisperse PP by the successive addition of the same amount of propylene.

MMAOs containing 0.4 mol% and 1.8 mol% of TIBA were prepared and abbreviated to dMMAO(0.4) and dMMAO(1.8), respectively. The results of post-polymerization of propylene with **2** activated by dMMAO(0.4) and dMMAO(1.8) illustrate that propylene polymerization proceeded in a living manner with **2**-dMMAO(0.4), whereas the M_n value of the second-step polymer obtained with dMMAO(1.8) system was almost the same with that of the first-step one. The results indicate that TIBA in dMMAO(1.8) worked efficiently as a chain transfer reagent only after all the propylene monomers had been consumed, and the new living polymer chains were generated by the addition of successive propylene monomers. To check the repeatability of this method, we continued third-step polymerization after the second-step. The conversion was quantitative, and the M_n value obtained was the same with that of the first-step polymer and consequently the *N* value became three times of that of first-step. We can conclude that the catalytic formation of monodisperse PPs was achieved with the present catalytic system in the presence of a suitable amount of TIBA[24].

The results of postpolymerization of norbornene contrasted markedly with those of propylene postpolymerization by **2**-dMMAO(1.8) where monodisperse PPs were catalytically obtained in the same conditions as described above. These results suggest the possibility of the catalytic synthesis of monodisperse block copolymers composed of norbornene and propylene with this catalytic system.

Block copolymerization with **2**-dMMAO(1.8) was than conducted as follows. The first-step polymerization was conducted with 0.35 g of norbornene for 7 min, and the second-step polymerization was successively conducted for another 30 min after the addition of 0.63 g of propylene. The results of the copolymerization are shown in Table 5.

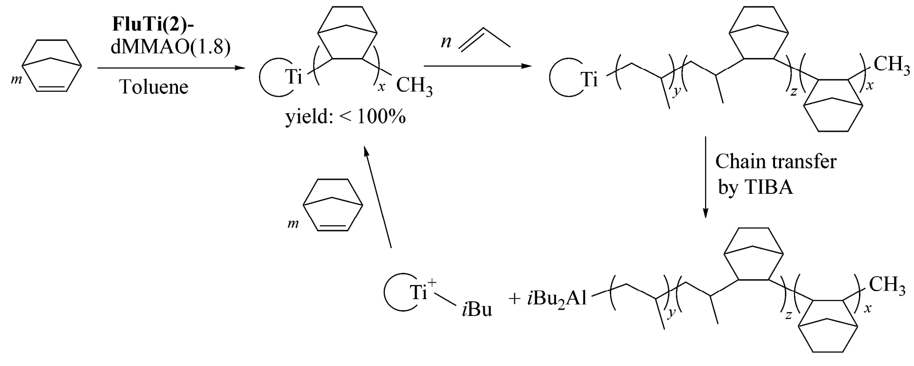
Table 5. Catalytic synthesis of block copolymers with **2**-dMMAO(1.8)[a]

Entry	Monomer	Time (min)	Yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$
20	NB	7	91	2.9	1.07
21	NB→P	7→30	100	12.8	1.13
22	NB→P→NB→P	7→30→7→30	100	12.9	1.18

[a] Polymerization conditions: Ti, 20 μmol, Al, 4.0 mmol; [b] Number average molecular weight and molecular weight distribution determined by GPC using polystyrene standards

Entry 20 shows the result of first-step polymerization of norbornene. The conversion reached to 91%, and the system gave the PNB with the M_n value of 29000 and the narrow MWD of 1.07. After the second polymerization, the conversion was almost quantitative, and the M_n value also increased against the yield with keeping narrow MWD (entry 21). The GPC curve of the polymer after the second step perfectly shifted to higher molecular weight region without the low molecular weight fraction of the prepolymer, which indicates the perfect formation of the block copolymer.

For the catalytic synthesis of this block copolymer, we repeated this block copolymerization (Scheme 1, entry 22). The conversion was quantitative, and the M_n value obtained was the same with that of the first block copolymer with the narrow MWD value. The GPC curve of the polymer obtained in the second block copolymerization was almost the same as that in the first block copolymerization (Fig. 5).



Scheme 1 Catalytic synthesis of block copolymer

These results indicate that the catalytic formation of monodisperse block copolymer was achieved with the **1**-dMMAO(1.8) system by the sequential additions of each monomer in the presence of a suitable amount of TIBA[25].

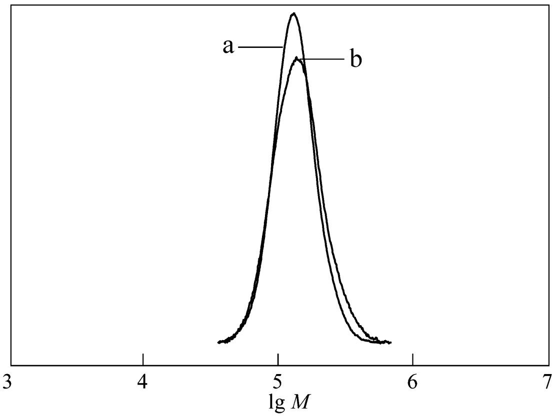


Fig. 5 GPC curves of block copolymers with **2**-dMMAO(1.8): (a) entry 21 and (b) entry 22

CONCLUSIONS

2-dMMAO system conducted living polymerization of propylene in heptane at 0 °C under various propylene pressure, where the syndiospecificity was controlled by the propylene pressure. This catalytic system was applied to the synthesis of syndiotactic-atactic stereoblock PP by changing propylene pressure and was found to give crystallizable di- and tri-stereoblock PPs. The catalytic system was also found to be effective for the living random copolymerization of norbornene with propylene and higher 1-alkens. The syndiotactic PP-*b*-poly(propylene-*ran*-norbornene) was prepared, which showed the melting point of syndiotactic PP and the glass-transition temperature of the random copolymer sequence, which were controllable according to the polymerization temperature and comonomer composition, respectively.

The catalytic system also gave monodisperse polypropylene in the presence of a suitable amount of TIBA, and the repeated addition of the same amount of propylene produced the polypropylene with the same molecular weight and molecular weight distribution because of the selective chain transfer after the monomer consumption. The successive addition of same amount of norbornene and propylene realized the catalytic synthesis of monodisperse block copolymer in this system. This concept should be applied to other living polymerization systems for the catalytic synthesis of tailor-made block copolymers by selecting a suitable chain transfer reagent and polymerization conditions.

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