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Preparation of Ultrahigh Molecular Weight Ethylene/1-Octene Block Copolymers Using Ethylene Pressure Pulse Feeding Policies

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Abstract: Ethylene pressure pulse feeding policies were employed in ethylene/1-octene living copolymerization with fluorinated FI-Ti catalyst. Ultrahigh molecular weight ethylene/1-octene block copolymers having hard-soft diblock structure and hard-soft-hard triblock structure were obtained. The soft blocks had high 1-octene content, while the hard blocks were mainly ethylene. The blocky structures were confirmed by NMR and high temperature GPC analyses. DSC measurements also showed that the hard blocks exhibited a high level of crystallinity and the soft blocks gave good low temperature flexibility. The block copolymers thus prepared have potential in thermoplastic elastomer applications.

Key Words: living polymerization, ethylene/1-octene copolymerization, olefin block copolymers, thermoplastic elastomer

Introduction

Precise control of polyolefin chain microstructure represents a major challenge in the polyolefin production. Over the past decades, great effort has been made in developing new catalysts for targeted chain microstructures.[1] It is well recognized that chain microstructure of polyolefins is determined by the type of catalysts used in olefin coordination polymerization. In contrast, the role of reaction engineering in determining chain microstructure is probably not as well known.[2] Using the same catalyst, reaction engineers can also control chain microstructural properties through the design of polymerization processes. An outstanding engineering example is the breakthrough development of Spherizone process.[3,4,5] In this process, a multistage sequential polymerization of propylene and then copolymerization of ethylene and propylene is conducted in a multizone circulating reactor (MZCR) using an appropriate Z-N catalyst system.[6] Composition, chain microstructure and thus material properties of PP/EPR in-reactor alloy products can be designed and regulated in a wide range.[7,8]

In the recent years, the advent of living olefin polymerization technique provides great opportunity for precise control of polyolefin chain microstructure, so as to tailor-make polyolefin materials.[9] Remarkable progresses have been achieved with the catalysts for living olefin polymerization.[10] Among living polymerization catalysts, fluorinated FI catalysts represent one of the most efficient systems.[11] Using a fluorinated FI-Ti catalyst, PE-b-PEP-b-sPP and PE-b-PEP-b-PE triblock copolymers were first synthesized by Fujita et al. through sequential addition of ethylene and propylene monomers.[12] Using another fluorinated FI-Ti catalyst, Coates et al. first synthesized iPP-b-PEP-b-iPP triblock copolymers, iPP-b-PEP-b-iPP-b-PEP-b-iPP pentablock copolymers, and iPP-b-PEP-b-iPP-b-PEP-b-iPP-b-PEP-b-iPP heptablock copolymers also via sequential monomer addition.[13] These novel block copolymers exhibited good elastomeric behavior and excellent extensibility and toughness.[14] Fujita et. al also synthesized PE-b-Poly(ethylene-co-1-hexene) diblock copolymers, which gave good extensibility and toughness.[15]. Recently, we investigated in a great detail the living copolymerization behavior of a fluorinated MFI-Ti catalyst in ethylene and 1-octene copolymerization.[16] Using this catalyst system, ethylene/1-octene diblock copolymers and gradient triblock copolymers with explicit block compositions were synthesized through sequential pulse feeding of the comonomer in semibatch living copolymerization.[17] It must be pointed out that olefin block copolymers can also be produced by chain shuttling polymerization (CSP), which has been successfully commercialized.[18,19] However, it should not limit the research and development of living olefin polymerization. Living polymerization technique requires only a single catalyst and microstructure of the chains can be well defined and controlled. It offers good controllability over the explicit chain microstructure. In comparison, CSP employs two post-metallocene catalysts and one reversible chain transfer agent (chain shuttling agent). One catalyst for ethylene/a-olefin copolymerization generates soft amorphous segments and the other catalyst mainly for ethylene homopolymerization generates hard semi-crystalline segments. Individual chains are shuttled between the two active centers through the chain shuttling agent, and thus the hard and soft segments are alternatively connected. The frequency and length of soft and hard segments in the multi-block copolymers are statistical.

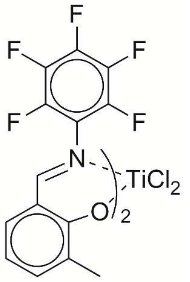
In living olefin copolymerization, sequential monomer feeding policies were proven to be powerful in the synthesis of various novel olefin block copolymers.[20,21,22] However, a general drawback with the living polymerization catalyst systems was their low rates of α-olefin consumption, such as 1-octene, 1-hexene, 1-butene or propylene. Fluorinated FI catalysts were extremely slow in incorporating α-olefins. A large excess amount of comonomer was thus added to assure an adequate comonomer feeding ratio f_2. It became greatly challenging to prepare block copolymers having clean successive blocks after comonomer addition in presence of the high concentration residual comonomer. This is why ethylene/α-olefin triblock copolymers with hard-soft-hard structure are seldom reported in the literature, in comparison to the study on ethylene/α-olefin hard-soft diblock copolymers.

It is well known that ethylene concentration in reactor can be easily regulated by ethylene pressure. While it is difficult to remove residual α-olefin comonomer during polymerization, ethylene concentration can be easily increased by increasing ethylene pressure. The increased ethylene concentration dilutes residual α-olefin comonomer and reduces the f_2 value in the synthesis of successive blocks. It is hypothesized that well-controlled ethylene/α-olefin block copolymers could thus be synthesized by design and operation of ethylene pressure profiles in living coordination copolymerization.

The objective of this work is to investigate ethylene pressure pulse feeding policies in the ethylene/1-octene living copolymerization. Ethylene/1-octene hard-soft diblock and hard-soft-hard triblock copolymers are synthesized and characterized.

Experimental Section

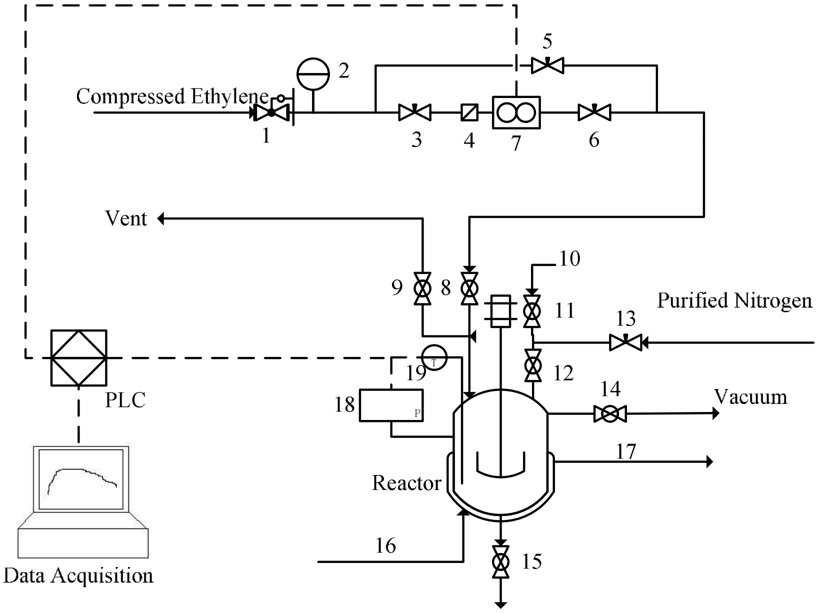
Materials and preparation: High purity nitrogen-filled glove-box and standard Schlenk technique were used in handling air- and/or moisture sensitive materials. Toluene (HPLC/Spectro grade, Tedia Company) was refluxed over potassium for at least 24 h before use. 1-Octene (99+%, Acros Organics) was distilled over sodium under nitrogen for 3 h and was then stored with molecular sieves in the glove-box. Polymerization-grade ethylene (Sinopec Yangzi Petrochemical Ltd) was purified by sequentially passing through columns filled with CuO, 5A molecular sieves and ascoarite. Methylaluminoxane (MAO), 10wt% Al in toluene from Albemarle, was first evaporated under vacuum at 50 °C, then washed twice with distilled n-hexane and finally dried in vacuum and stored as white powder in the glove-box (dried MAO, dMAO).[23,24] The catalyst precursor used in this work was bis[N-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium(IV) dichloride, which was synthesized following the literature procedure.[25] The catalyst structure is shown in Scheme 1.



Scheme 1. The structure of fluorinated FI-Ti catalyst used in this work.

Ethylene/1-octene copolymerization: The ethylene and 1-octene copolymerization runs were carried out in a one-liter autoclave reactor system, as shown in Scheme 2. The reactor was installed with an anchor impeller rotating at 300 rpm. The reactor temperature was controlled at 25 ℃ through jacket cooling water. Prior to use, the reactor was thoroughly dried at 90 ^{o}C by repeatedly evacuating and refilling with nitrogen at least for six hours. The temperature was then decreased to 25 ^{o}C and filled with pure ethylene. The toluene solutions of catalyst and cocatalyst dMAO were freshly prepared prior to each experiment. The agitation was set at 300 rpm, followed by opening the nitrogen valve 13. With the valves 11 and 12 opened, the solvent, comonomer, cocatalyst and catalyst solution was sequentially injected into the reactor quickly through the liquid inlet connector 10, under the protection of nitrogen. Once the catalyst solution was injected, the liquid inlet valves 11 and 12 were shut off in 10 seconds, and the gas inlet valve 8 was opened immediately. Ethylene was fed continuously to maintain the required pressure during the reaction.

The ethylene pressure was controlled by the pressure regulator 1 in the ethylene feeding pipeline. To synthesize block copolymers, ethylene pressure in the reactor was increased in a stepwise fashion, following the designed feeding policy. After the preset reaction time, the polymerization was terminated by shutting off the gas inlet valve 8. For high pressure reactions, the gas exhaust valve 9 was opened to vent the reactor before opening the discharge valve 15. The resulting mixture was immediately poured into acidified alcohol (2 vol.% of hydrochloric acid). The polymer sample was washed with excess alcohol, and finally dried in vacuum at 50 ^{o}C for 8 h after filtration.



Scheme 2. Semi-batch reactor system for high pressure polymerization of olefins: 1,8: regulator; 2: pressure gauge; 3,5,6,13: needle valve; 4: filter; 7: ethylene mass flow controller; 8: gas inlet ball valve; 9: gas exhaust ball valve; 10: liquid inlet connector; 11,12: liquid inlet ball valve; 14: evacuation ball valve; 15: discharge valve; 16: jacket cooling water inlet; 17: jacket cooling water outlet; 18: pressure transducer; 19: temperature transducer.

Polymer characterization: The detailed characterization of copolymer molecular weight, composition and DSC properties has been described in our previous paper.[16,17] It is briefly summarized here for the readers' convenience. Molecular weight (M_w and M_n) and polydispersity index (PDI) of the copolymers were analyzed by high temperature PL-GPC 220 system. Monodisperse polystyrene (PS) standards were used for calibration. The Mark-Houwink constants for the universal calibration were $K = 5.91\times10^{-4}$ and $\alpha = 0.69$ for PS, and $K = 1.21\times10^{-4}$ and $\alpha = 0.707$ for PE. 1,2,4-Trichlorobenzene as solvent was pumped at a flow rate of 1.0 ml/min at 150 ^{o}C.

The copolymer composition was determined by ^{13}C NMR spectra. Copolymer solutions with 10 wt% in deuterated o-dichlorobenzene were prepared at 150 ^{o}C and scanned at 125 ^{o}C using a Bruker AC 400 pulsed NMR spectrometer. Special instrument conditions included: 90^{o} pulse angle, inverse gated proton decoupling, 8 s pulse delay time, 1.3 s acquisition time and approximate 5000 scans. The carbon assignments and the composition calculation followed the ASTM D5017-96 method.[26]

The thermal properties of the copolymers were measured by TA Q200 thermal analyzer under N_2

atmosphere. Samples of 5.0~7.0 mg were first heated up to 160 ^{o}C and remained isothermly at 160 ^{o}C for 5 min to remove the thermal history. Recrystallization was achieved by cooling the samples to -90 ^{o}C at 10 ^{o}C /min. The samples were reheated from -90 to 160 ^{o}C at 10 ^{o}C /min after isotherm at -90 ^{o}C for 3 min. The cooling curve was used for determing the temperature of crystallization (T_c), and the second heating curve for the glass transition temperature (T_g) and peak melting temperature (T_m).

Results and Discussion

Synthesis of ethylene/1-octene block copolymers

Table 1 summarizes the experimental conditions and results. Runs 1~3 were carried out as the control experiments. A two-stage polymerization process was applied in Runs 4~9. Figure 1 shows the monomer feeding policy of Run 9 as an example. In the first stage, the ethylene pressure in the reactor was maintained at 1.2±0.1 bar for 3 min, with the comonomer feeding ratio f_2 as high as 0.90, which would produce a soft poly(ethylene-co-1-octene) block with high 1-octene incorporation. In the second stage, the ethylene pressure was instantaneously increased to 20±0.1 bar, the f_2 value in the reaction system was therefore decreased to about 0.28, which would produce a relatively hard block with low 1-octene incorporation. The reaction was stopped after 2.5 min for the second stage. This ethylene pressure pulse feeding policy resulted in soft-hard diblock copolymers with soft block synthesized first, in contrast to the hard block first synthesis using a comnomer sequential feeding policy.[17]

In Run 10, a three-stage polymerization process was performed, combining the ethylene pulse feeding together with 1-octene pulse feeding. As shown in Figure 2, the polymerization was first performed at an ethylene pressure of 1.2±0.1 bar for 2 min (f_2 = 0.33). It was followed by a quick injection of 120 ml 1-octene while the ethylene pressure remained constant (f_2 = 0.90). The second stage was lasted for 5 min. The ethylene pressure was then instantaneously increased to 20±0.1 bar

(f_2 = 0.28). The third stage was continued for 1.5 min before termination. This three-stage polymerization process resulted in hard-soft-hard triblock copolymers.

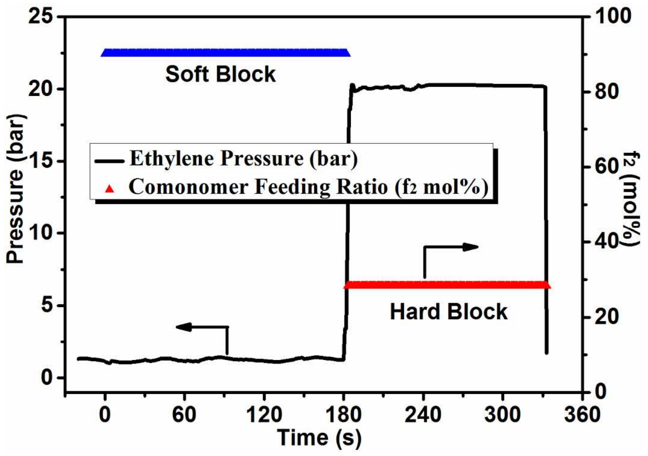


Figure 1. Ethylene pressure profile and comonomer feeding ratio f_2 in the two-stage polymerization of ethylene and 1-octene (Run 9), targeting for hard-soft diblock copolymers.

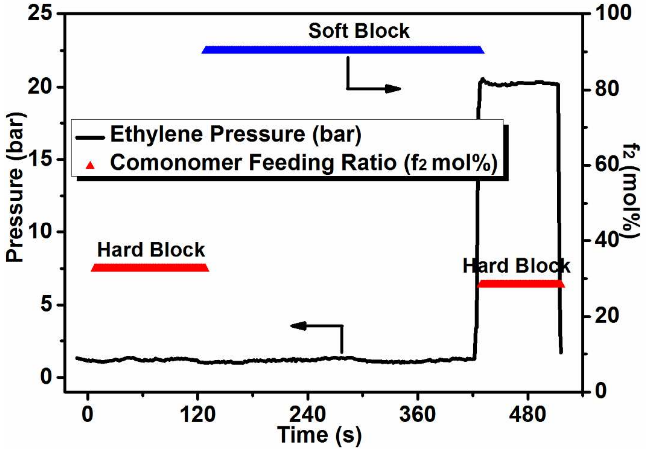


Figure 2. Ethylene pressure and comonomer feeding ratio f_2 in the three-stage polymerization (Run 10), targeting for hard-soft-hard triblock copolymers.

Table 1. Conditions and results of the synthesis of olefin block copolymers through ethylene pressure pulse method.

Run [a]	Copolymer Type	Ethylene Pressure(bar)	f_2 [b]	Time (min)	Yield (g)	Activity [c]	$\overline{F}_2$ [d] (mol%)	M_w [e] (10^4g/mol)	PDI [e]	T_m [f] (℃)	T_g [f] (℃)	T_c [f] (℃)	ΔH [f] (J/g)	X_c [g] (%)
1	random	1.2	0.90	5	3.98	3.18	18.7	24.54	1.14	26.7	-61.8	8.3	25.4	9
2	random	1.2	0.90	10	7.60	3.04	19.8	43.70	1.24	23.0	-61.6	5.0	30.5	10
3	random	20	0.28	1	6.49	25.95	5.2	46.82	1.44	99.7	-40.9	84.2	60.2	20
4	diblock	1.2+20	0.90+0.28	5+0.5	6.39	4.65	12.3	42.45	1.16	78.7,24.3	-61.6	60.6,2.9	47.0	16
5	diblock	1.2+20	0.90+0.28	10+0.5	9.79	3.73	13.1	57.04	1.58	85.8,22.4	-61.3	67.3,7.6	43.0	15
6	diblock	1.2+20	0.90+0.28	5+1	10.72	7.15	9.5	65.85	1.48	88.3	-60.4	74.0	58.6	20
7	diblock	1.2+20	0.90+0.28	10+1	11.04	4.01	13.6	83.54	1.17	82.4,31.5	-61.2	64.2,12.5	47.2	16
8	diblock	1.2+20	0.90+0.28	6+2	27.55	12.24	6.3	115.45	1.30	98.9	-59.6	81.2	58.9	20
9 [h]	diblock	1.2+20	0.90+0.28	3+2.5	19.85	21.65	7.8	187.01	1.49	87.8	-62.7	74.0	52.4	18
10 [i]	triblock	1.2+1.2+20	0.33+0.90+0.28	2+5+1.5	14.12	6.64	8.0	111.01	1.63	83.9	-53.5	67.1	45.2	15

a: polymerization conditions: Ti = 15 μmol, dMAO as cocatalyst, Al/Ti = 2000, polymerization temperature = 25 °C, toluene = 330 ml, stir rate = 300 rpm, b: the feeding molar ratio of 1-octene; c: average activity, 10^6g/(mol Ti·h); d: average 1-octene molar incorporation in the copolymer, determined by high temperature ^{13}C NMR, e: determined by high temperature GPC; f: determined by DSC; g: crystallinity from heat of melting, $X_{C,DSC} = \Delta H_m/\Delta H_m^0$, $\Delta H_m^0 = 293$ J/g; h: Ti = 10 μmol; i: polymerization was first performed at ethylene pressure of 1.2±0.1 bar with only 5 ml 1-octene for 2 min, then 120 ml 1-octene was added quickly to continue the reaction for 5 min with ethylene pressure remaining constant, finally the ethylene pressure was instantaneously increased to 20±0.1 bar for another 1.5 min.

All the copolymers synthesized in this work exhibited narrow molecular weight distributions, demonstrating good living behavior in the stage-wise ethylene pressure pulse feeding process. The increases in the copolymer molecular weight from Runs 1~3 in the stage-wise processes were evident in Table 1 and in Figure 3. The chain extension obviously occurred in the second stage at the high ethylene pressure. In the three-stage polymerization process (Run 10), the weight-average molecular weight after the second stage was about 445 kg/mol.[27] After the third stage, the total molecular weight reached 1110 kg/mol, and the PDI value was only about 1.6, demonstrating substantial extension of the copolymer chains at the third stage. The molecular weights in Runs 8~10 were ultrahigh, over one million.

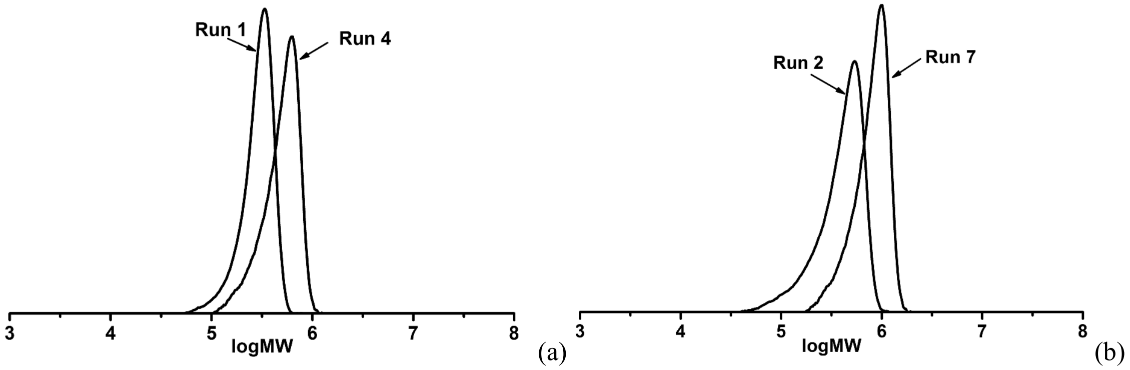


Figure 3. Comparison of the GPC curves showing chain extension: (a) Run 1 vs. Run 4, (b) Run 2 vs. Run 7.

As listed in Table 1, the ^{13}C-NMR analysis showed that the average comonomer incorporation $\overline{F}_2$ in the copolymers synthesized from the stage-wise polymerization (Runs 4~10) was lower than that from the single-stage polymerization, which only produced the soft random copolymer at low ethylene pressure (Runs 1&2), but was higher than the hard random copolymer synthesized at high ethylene pressure (Run 3). The $\overline{F}_2$ value in the second chain block (the third block in Run 10) was lower than the first block. Figure 4 shows the differences of the comonomer incorporation. Take

Figure 4a as an example for illustration, the reaction condition in Run 1 was the same as that in the first stage polymerization of Runs 4&6, which meant the average 1-octene incorporation in Run 1 was the same as that in the first soft block of Runs 4&6. The reaction pressure in Run 3 was the same as that in the second stage polymerization of Runs 4&6, giving the same average 1-octene incorporation in Run 3 as that in the second hard block of Runs 4&6. Therefore, the total average 1-octene incorporation of Runs 4&6 was lower than Run 1, but higher than Run 3, as shown in Figure 4a. This was also confirmed by comparison of the triad sequence length distributions of the copolymers, which was listed in Table 2.

The evolution of molecular weight and comonomer incorporation clearly demonstrated the successful synthesis of ethylene/1-octene diblock copolymers through the stage-wise ethylene pressure pulse feeding policy. Also demonstrated in Run 10 was the synthesis of a hard-soft-hard triblock copolymer through combining 1-octene pulse feeding and ethylene pressure pulse feeding. To our knowledge, this represents the first synthesis of ethylene/1-octene diblock and hard-soft-hard triblock copolymer samples through an ethylene pressure pulse feeding policy.

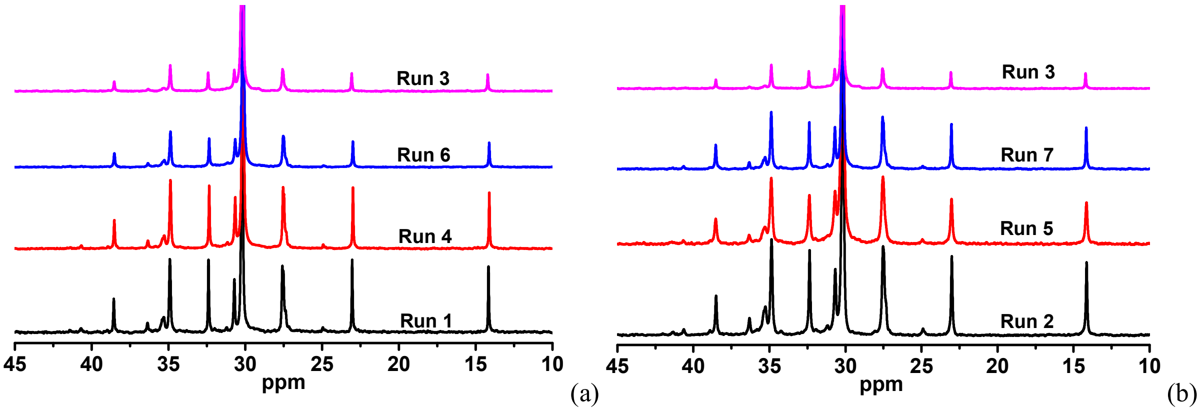
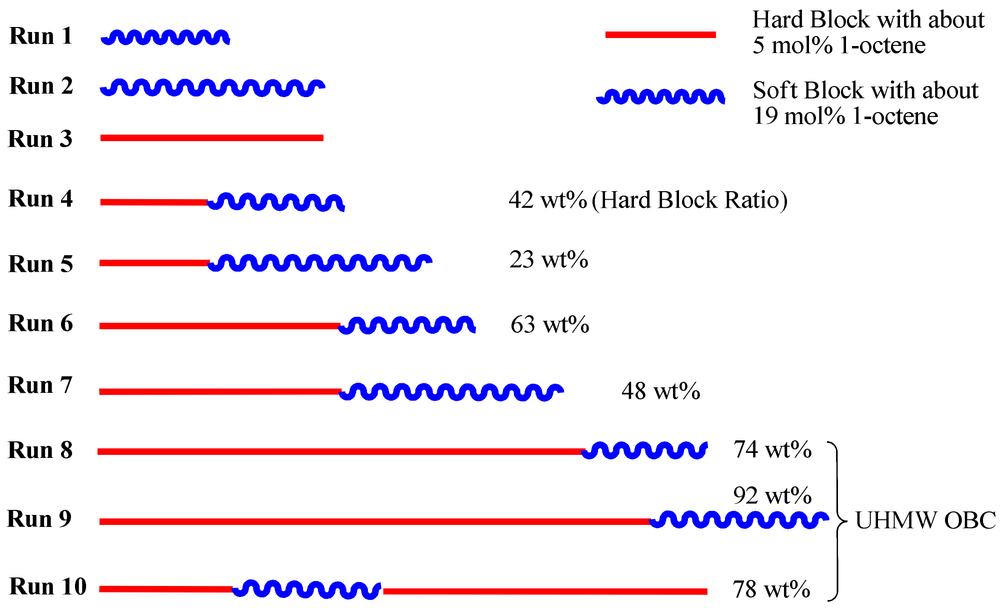


Figure 4. Comparison of the ^{13}C-NMR spectra: (a) Runs 1&3 vs. Runs 4&6; (b) Runs 2&3 vs. Runs 5&7.

Table 2. The triad sequence length distributions for ethylene/1-octene copolymers determined by ^{13}C-NMR.

Run No.	EEE (%)	EEO+OEE (%)	OEO (%)	EOE (%)	EOO+OOE (%)	OOO (%)
1	57.07	20.89	3.22	12.65	6.17	0
2	57.30	19.70	2.68	13.18	7.15	0
3	89.13	4.98	0.36	4.13	1.39	0
4	74.79	10.24	2.19	9.20	3.59	0
5	70.35	14.58	2.06	9.23	3.78	0
6	80.71	9.54	1.00	6.20	2.55	0
7	65.80	18.12	2.38	10.43	3.26	0
8	88.11	5.64	0.41	4.41	1.43	0
9	78.78	12.62	1.11	5.80	1.70	0
10	75.92	14.95	1.05	6.15	1.92	0

The chain structures of the copolymers synthesized in this work through the ethylene pressure pulse method are schematically presented in Scheme 3. The hard block ratios in the block copolymers were estimated from the total molecular weight of the block copolymers in reference to those obtained from the control experiments (Runs 1~3). Run 4 and Run 5 samples possessed similar hard block lengths, for the two run had the same ethylene pressure pulse feeding time duration. Run 4 and Run 6 samples had similar soft block lengths, for the runs had the same reaction time in the first stage. Run 7 sample had a similar hard block length as Run 6 and similar soft block length as Run 5. Runs 8, 9 and 10 demonstrated that, through the ethylene pressure pulse feeding policy, ultra-high molecular weight ethylene/1-octene copolymers with blocky structures could be synthesized by the living coordination polymerization.



Scheme 3. Schematic structures of the block copolymers made by ethylene pressure pulse method.

Thermal properties of the block copolymers

Basic thermal properties of the block copolymers were studied by DSC, in comparison with their random copolymer counterparts. The T_m, T_g and T_c results are included in Table 1. The T_m values of the block copolymers prepared by the ethylene pressure pulse feeding (Runs 4~10) were lower but close to the corresponding hard random copolymer from Run 3. The T_g values of the block copolymers were around -60 ^{o}C, similar to the soft random copolymers from Runs 1&2. The block copolymers possessed the ability of crystallization of the hard block and the low temperature flexibility of the soft block.

Figure 5 shows the DSC melting and cooling curves. In Runs 4, 5 and 7, the soft blocks dominated the copolymer chains in mass, leading to the broad or bimodal distributions in the DSC melting and cooling curves. In the other block copolymer samples, the hard block contents were significantly higher than the soft blocks. The melting and crystallization enthalpies of the soft blocks were not detectable in these DSC melting and cooling curves, rendering the unimodal distributions. It should be pointed out that the T_m values of the block copolymers made by the ethylene pressure pulse feeding in this work were lower than those reported for the sequential comonomer feeding policy,[15,17] and also lower than the commercial OBC's produced by the chain shuttling polymerization technique.[28] Further increase in the ethylene pressure is required to reduce 1-octene content in the hard blocks.

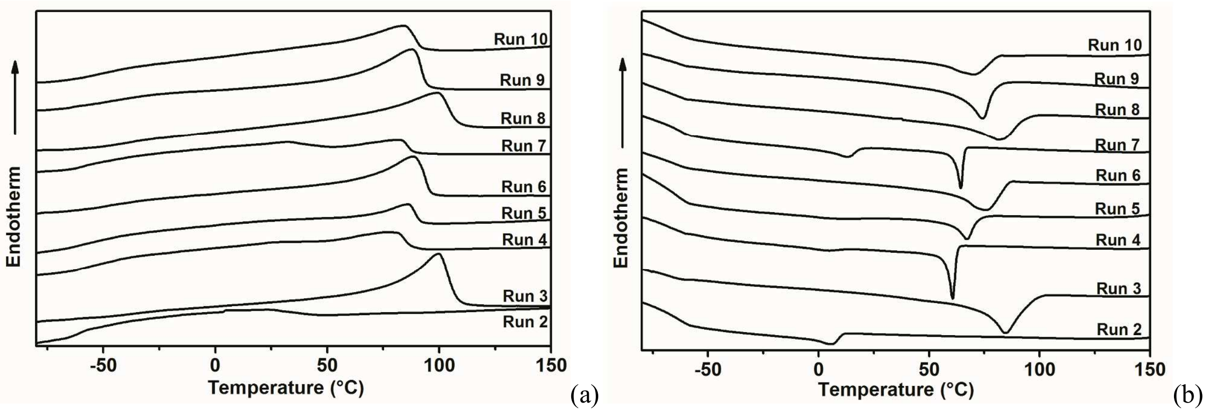


Figure 5. DSC analysis of the ethylene/1-octene block copolymers in comparison their corresponding random copolymer counterparts, (a) melting curves, (b) cooling curves.

Conclusion

A series of ethylene/1-octene diblock and triblock copolymers were synthesized in this work, with a fluorinated FI-Ti catalyst system by employing ethylene pressure pulse feeding policies. The soft block of the synthesized diblock copolymers had about 19 mol% 1-octene incorporation while the hard block contained only 5 mol% 1-octene. Ethylene/1-octene triblock copolymer had two hard blocks at the chain ends and one soft block at the middle. The blocky structures were demonstrated by the NMR and high temperature GPC analyses. The block copolymer samples had ultra-high molecular weight over one million. DSC analysis showed that the hard block possessed good ability of crystallization, while the soft block gave good low temperature flexibility, rendering the block copolymers high potential applications in the area of thermoplastic elastomers.

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References and Notes

1. D. Takeuchi, *Dalton Trans.,* 2010, 39, 311-328.
2. S. Zhu, A. Hamielec, in *Polymer Science: A Comprehensive Reference,* ed. K. Matyjaszewski and M. Möller, Elsevier, Amsterdam, 2012, pp. 779-831.
3. G. Covezzi, G. Mei, *Chem. Eng. Sci.,* 2001, 56, 4059-4067.
4. G. Mei, P. Herben, C. Cagnani, A, Mazzucco. *Macromol. Symp.*, 2006, 677, 245-246.
5. J.C. Chadwick, *Macromol. React. Eng.*, 2009, 3, 428-432.
6. Z. Tian, X.P. Gu, G.L. Wu, L.F. Feng, Z.Q. Fan, G.H. Hu, *Ind. Eng. Chem. Res.*, 2011, 50, 5992-5999.
7. Q. Dong, X.F. Wang, Z.S. Fu, J.T. Xu, Z.Q. Fan, *Polymer*, 2007, 48, 5905-5916.
8. Z. Tian, X.P. Gu, G.L. Wu, L.F. Feng, Z.Q. Fan, G.H. Hu, *Ind. Eng. Chem. Res.*, 2012, 51, 2257-2270.
9. Z. Ye, L. Xu, Z. Dong, P. Xiang, *Chem Commun.*, 2013, 49, 6235-6255.

10. G.J. Domski, J.M. Rose, G.W. Coates, A.D. Bolig, M. Brookhart, *Prog. Polym. Sci.*, 2007, 32, 30-92.
11. H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.*, 2011, 111, 2363-2449.
12. M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc*., 2002, 124, 3327-3336.
13. J.B.Edson, Z. Wang, E.J. Kramer, G.W. Coates, *J. Am. Chem. Soc.*, 2008, 130, 4968-4977.
14. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G.H. Fredrickson, E.J. Kramer, Y.W. Shin, F. Shimizu, A.E. Cherian, P.D. Hustad, J. M. Rose, G.W. Coates, *PANS*, 2006, 103, 15327-15332.
15. R. Furuyama, M. Mitani, J. Mohri, R. Mori, H. Tanaka, T. Fujita, *Macromolecules*, 2005, 38, 1546-1552.
16. W. Liu, K. Zhang, H. Fan, W.J. Wang, B.G. Li, S. Zhu, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, 51, 405-414.
17. W. Liu, S. Guo, H. Fan, W.J. Wang, B.G. Li, S. Zhu, *AIChE J.*, 2013, 59, 4686-4695.
18. D.J. Arriola, E.M. Carnahan, Y.W. Cheung, D.V. Devore, D.D. Graf, P.D. Hustad, WO Int. Pat., 090427, 2005.
19. D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, *Science,* 2006, 312, 714-719.
20. L. Pan, M. Hong, J.Y. Liu, W.P. Ye, Y.S. Li, *Macromolecules*, 2009, 42, 4391-4393.
21. S.M. Yu, S. Mecking, *J. Am. Chem. Soc.*, 2008, 130, 13204-13205.
22. L.P. He, J.Y. Liu, Y.G. Li, S.R. Liu, Y.S. Li, *Macromolecules*, 2009, 42, 8566-8570.
23. Z. Cai, T. Ikeda, M. Akita, T. Shiono, *Macromolecules*, 2005, 38, 8135-8139.

24. K. Itagaki, K. Kakinuki, S. Katao, T. Khamnaen, M. Fujiki, K. Nomura, S. Hasumi, *Organometallics*, 2009, 28, 1942-1949.

25. M. Mitani, R. Furuyama, J.I. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, T. Fujita, *J. Am. Chem. Soc.*, 2003, 125, 4293-4305.

26. ASTM D5017-96, West Conshohocken, e1, 2009.

27. In Run 10, the weight average molecular weight after the first stage was about 200 kg/mol. This data could be found in our previous work in Ref. 17. The molecular weight obtained in the second stage was assumed to be similar to that of Run 1 in this work, that was 245.4 kg/mol. Thus, the total weight average molecular weight after the second stage was estimated to be about 445 kg/mol.

28. H.P. Wang, D.U. Khariwala, W. Cheung, S.P. Chum, A. Hiltner, E. Baer, *Macromolecules*, 2007, 40, 2852-2862.