Comparison of Thermal Properties of Ethylene-Norbornene Copolymers Prepared by Batch and Semi-Batch Processes

Shaojie Liu,[1] Zhen Yao,[1] Kun Cao[1,2]

[1]State Key Laboratory of Chemical Engineering (ZJU), Institute of Polymerization and Polymer Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China
[2]State Key Laboratory of Chemical Engineering (ECUST), UNILAB Research Center of Chemical Reaction Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

ABSTRACT: Ethylene-norbornene copolymers (ENCs) with various norbornene (NB) fractions could be synthesized by metallocene catalyst in both batch and semi-batch processes. The batch process with long reaction time produced the ENC samples having considerable copolymer composition drift (CCD) while the semi-batch process yielded narrow CCD. Furthermore, the effects of CCD on the resultant ENC's thermal properties were discussed. It was found that the thermal properties were dependent on both the NB fraction in obtained ENC and its CCD. The work demonstrated the importance of controlling CCD in the production of ENCs for superior materials properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2493–2496, 2009

Key words: cyclic olefin copolymer; ethylene; norbornene; metallocene catalyst; batch; semi-batch

INTRODUCTION

Ethylene-norbornene copolymer (ENC) has been an important olefins polymer material for its excellent properties and broad applications.[1–6] The study on ethylene and norbornene (NB) copolymerization with homogeneous metallocene catalysts has been carried out by many researchers.[1–25] The glass transition temperature (T_g) of ENC increases with the NB content in the copolymer and the linear relationships between T_g and NB fractions have been reported.[1,4,6,16–18]

However, the ENCs with similar NB contents could exhibit different T_g. Harrington and Crowther[19] reported that the random and alternating copolymers with similar NB contents had significantly different T_g. The alternating copolymers had lower T_g compared with their random counterparts. Forsyth et al.[20] studied the influence of the polymer microstructure on the thermal properties of ENCs with high NB contents. The results indicated that there is no linear correlation between the amounts of NB incorporated in copolymers and thermal properties while copolymers containing high NB contents and different microstructures. Pereña and coworkers[21] described the effect of the molecular weight on the thermal properties of ENCs. It has been found that the values of T_g for the copolymers with same NB contents increased significantly with increasing average number molecular weight up to a limit of 6–10 $\times 10^4$ g/mol. In these studies, the copolymerization was generally carried out at a low total conversion to minimize the copolymer composition drift (CCD) effect.

The qualitative analysis on the effect of CCD on the thermal property of ENC has been reported by Choi and coworkers.[8] The T_g of obtained copolymer decreased with the reaction time increasing for the composition drift. This research inspired us to explore the influence of the CCD on the thermal property of ENC.

The range of CCD should be mainly determined by the production approaches. The approaches for ENCs can be divided into batch, semi-batch, and continuous techniques based on the NB feeding strategies. The semi-batch process can be further classified to interval impulse feeding and continuous feeding. Using continuous process to produce ENC with uniform composition has been reported by Choi and coworkers.[8] In our previous work, we applied semi-continuous process to achieve the same objective.[25] In this article, we synthesized ENC samples by batch process and semi-batch process including impulse feeding and continuous feeding and compared the thermal properties of ENCs obtained by these processes.

Correspondence to: Z. Yao (yaozhen@zju.edu.cn) and K. Cao (kcao@che.zju.edu.cn).

Copolymerization of Ethylene and NB Based on Different NB Feeding Approaches Between Batch and Semi-Batch Processes

Run	NB/E ($t = 0$)	Polymerization process	Reaction time (min)	NB in ENCs (mol %)	T_g (°C)	ΔT_g (°C)	T_m (°C)
1	1.5	Batch	8	23.5			–
			10	20.4			119
2	15.0	Semi-batch (Impulse feeding)	30	53.5	141	24	–
			60	52.6	141	24	–
3	12.3	Semi-batch (Continuous feeding)	30	53.1	144	18	–
4	9.0	Batch	73	36.8	82	25	123
5	1.0	Batch	10	17.6			121
6	0.6	Semi-batch (Continuous feeding)	30	17.2			–

Catalyst concentration $= 4 \times 10^{-5}$ mol/L.
Al/Zr $= 1500$; Toluene $= 50$ mL; P $= 1$ atm; T $= 70°$C.

EXPERIMENTAL SECTION

Materials

Ethylene with 99.95% purity was further purified by passing through columns filled with 3Å molecular sieves and Cu catalysts before entering the reactor. NB (from ACROS) was dried over CaH_2 before use. Toluene as AR grade was dried over a sodium/potassium alloy before use; rac-[Et(Ind)$_2$]ZrCl$_2$ was purchased from ACROS and used as received. Methylaluminoxane (MAO) was 10 wt % solution in toluene and provided by AKZO NOBEL.

Polymerization

The general procedure was similar to that reported in our previous article.[23] All runs were carried out in a 100 mL glass flask under atmospheric pressure at 70°C and the Al/Zr mole ratio was 1500. During the polymerization process, ethylene was continuously fed into the reactor for maintaining the atmospheric pressure. NB was added following the designed feeding approaches, which the given NB solution with toluene should be injected at regular time intervals by a pulse pump in impulse feeding method and continuously added by a peristaltic pump in continuous feeding method.

Characterization and measurements

The copolymer composition was measured by Varian Unity-400 nuclear magnetic resonance instrument. The copolymer shift assignments and calculations followed the analysis method of Ruchatz and Fink.[3] The thermal properties of copolymers were measured using Perkin–Elmer DSC 7. All the samples were scanned between 30°C and 200°C at 10°C/min. The second heating and first cooling curves were applied.

RESULTS AND DISCUSSION

All runs using different NB feeding strategies in this work were summarized in Table I.

Figure 1 showed the DSC curves for the resulting ENCs with low NB fractions prepared by the batch process. An interesting observation was that the copolymer materials changed from amorphous to crystalline when the reaction time varied from 8 to 10 min. The crystal formation in the 10-min sample was resulted from the CCD and then the latter obtained ENC with very low NB content should be considered. Because the NB content was so low, some long polyethylene sequences that could lead to crystallization were formed.

Therefore, the CCD can be dramatic in the batch process along with the reaction time, and then the ENC with broad CCD will be produced. The effect
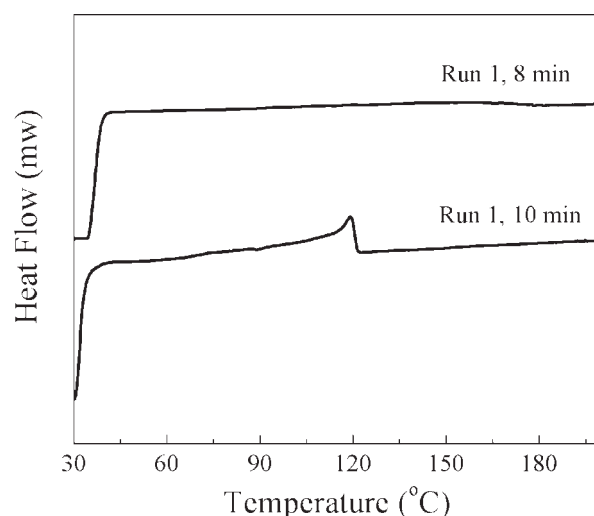

Figure 1 DSC curves of the ENCs obtained by Run 1 with low initial concentration of NB at different reaction times in batch copolymerization.
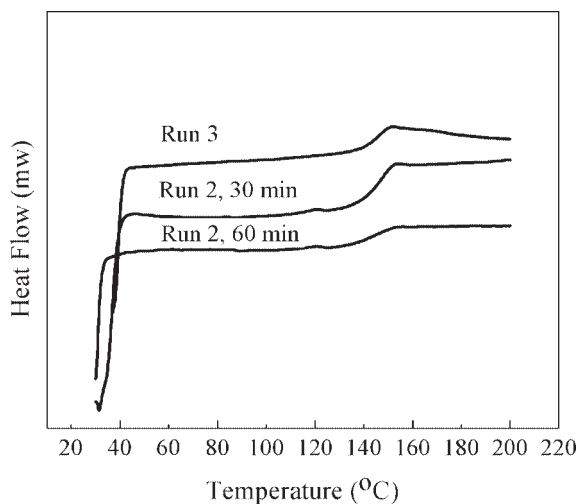
Figure 2 DSC curves of the ENCs obtained by Run 2 and 3 using different feeding approaches of NB at different reaction times in semi-batch copolymerization.

Figure 4 DSC heating and cooling curves of the ENC with low NB fraction and broad CCD obtained by Run 5 in batch copolymerization.

of broad CCD on the ENC's thermal properties becomes clear.

To further investigate the effect of CCD on the ENC thermal properties, various samples with narrower CCD but similar NB fractions in the ENCs were prepared using the semi-batch process. Except for the initially charged NB, the amount of NB was added during the reaction process using both impulse feeding and continuous feeding approaches. Figure 2 showed the comparison of T_g of the resultant ENCs with the high NB fractions prepared by semi-batch processes. For Run 2, certain amounts of NB were added in pulse at the 30 min and 45 min to control its CCD in the range of that by batch process in the 30 min when the reaction time was extended to 60 min. For Run 3, the additional NB
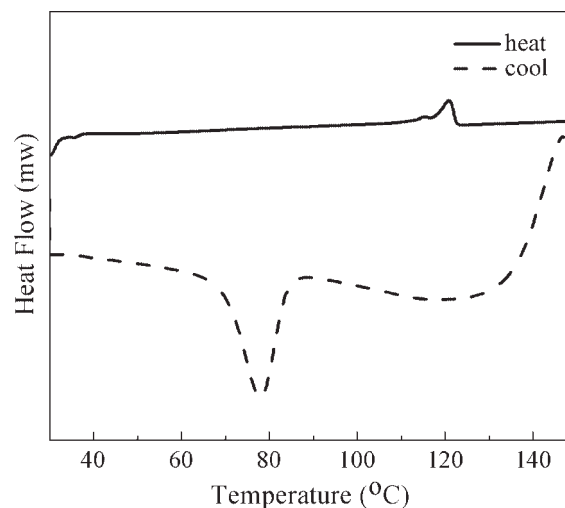
was continuously added at the given rate during 30 min, trying to obtain ENC with very narrow CCD. These resulting ENCs had similar average NB fractions from 52.6 to 53.5%. The major differences should be their CCD. It could be seen that the sample with the narrow CCD obtained from the semi-batch process (Run 3) gave the narrow range of glass transition. When the CCD became broader (Run 2), the range of transition was wider. Therefore, T_g of Run 2 sample became slightly lower than Run 3 sample. In other words, the copolymer with narrower CCD should have better thermal properties than the ones with the same average composition but broader CCD. The DSC curves of the samples from Run 2 in 30 min and 60 min were very similar. This may be due to their similar CCD because the
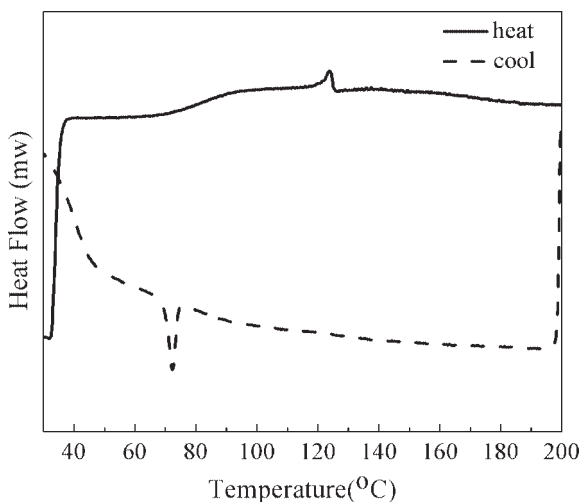

Figure 3 DSC heating and cooling curves of the ENC with moderate NB fraction and broad CCD obtained by Run 4 in batch copolymerization.
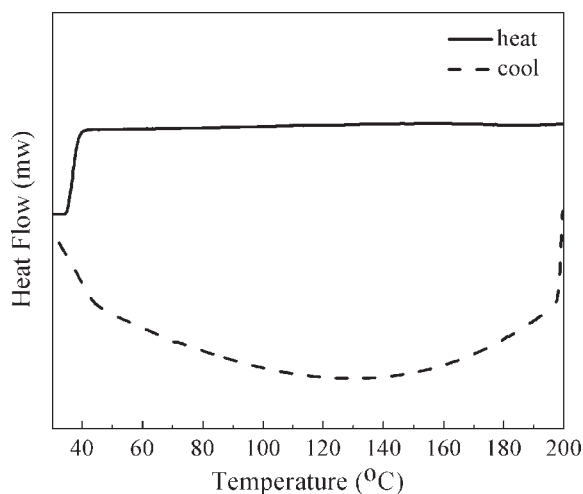

Figure 5 DSC heating and cooling curves of the ENC with low NB fraction and narrow CCD obtained by Run 6 in semi-continuous copolymerization.

latter prevented the unilateral decrease of NB concentration in the polymerization system based on the stepwise addition of NB in the latter stage of copolymerization. This observation confirmed that the thermal properties of obtained ENCs should be strong dependence on their CCD.

Figures 3–5 showed the comparison for the samples with low NB contents between batch and semi-batch processes. It was found that the copolymers with narrow CCD prepared by the semi-batch process (Run 6) were amorphous, even if the average NB content was only 17.2%. However, although the average NB content of copolymers obtained from the batch process (Run 4) was 36.8%, they were crystalline because of dramatic composition drift. Reasonably, Run 5 sample by batch process with average 17.6% NB fraction was also crystalline. These results clarified that the thermal properties were dependent on both the NB fraction in obtained ENC and its CCD.

CONCLUSIONS

The NB addition policy showed a significant effect on the thermal properties of the obtained ENCs. The batch process resulted in broad CCD that lowered T_g, broadened the range of glass transition, and even yielded crystallization due to a wider composition drift during the copolymerization. The ENCs having similar average NB contents but narrow CCD prepared by the semi-batch process exhibited very narrow glass transition, especially in the semi-continuous process. In particular, the ENCs with low NB contents by the batch process contained chains of very low NB and thus became crystalline materials. In contrast, the samples prepared by the semi-continuous process were amorphous due to their narrow CCD.

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