

Polyethylene Fractionation by Modified Temperature Rising Elution Fractionation Technique

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Abstract

Though Temperature Rising Elution Fractionation (TREF) has been known as the most effective method for polyolefin fractionation, such as PE and PP. These polymers are semicrystalline and show various degrees of branching distribution which affects on their solubility. Unfortunately the drawback of preparative TREF is time-consuming, particularly, in the crystallization step. To solve this problem, mixed solvent for crystallization has been attempted. LLDPE resins produced commercially from ethylene and various comonomer such as 1-butene, 1-hexene and 1-octene were used in this study. It was found that the total analysis time depended on the strength of solvent used in the crystallization step.

Keywords: Short chain branching distribution, Polyethylene, TREF, Ethylene/ α -olefin copolymers

1. Introduction

Currently, linear low density polyethylene (LLDPE) is one of the most widely produced polymers in the world. The applications of LLDPE resins are very diverse and various LLDPE types are in use. The diversity of LLDPE types is a result of large variations in molecular structure such as molecular weight distribution (MWD), the average molecular weight and short chain branching distribution (SCBD). Especially, short chain branching [1-3] in the structure of LLDPE affects many physical and mechanical properties [4,5] such as rigidity density hardness permeability tensile strength and storage-loss moduli. To determine the compositional heterogeneity for polyolefins, Temperature Rising Elution Fractionation (TREF) is the most efficient technique [6-8]. Generally, TREF is composed of two sequential steps as described in Fig. 1, namely crystallization and elution. In the first step, the polymer is dissolved in a suitable solvent and then put in contact with an inert support. The crystallization is carried out under well controlled condition by slowly decreasing the temperature. In the elution step, solvent flows through a column packed which the polymer coated the inert support while the temperature is raised stepwise at an interval.

Recently, there are many research used the preparative TREF to determine short chain branching density of ethylene/ α -olefin copolymers which used the long time in the crystallization step. Since the cooling rate is mostly about 1.0-2.0 °C/h, the crystallization time is time-consuming [6,7] too. Not only time-consuming, but also wastes the power of heat.

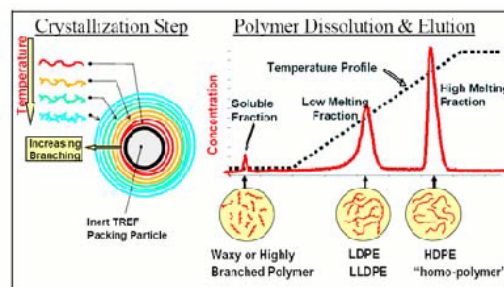


Fig. 1: Mechanism of TREF (reproduced from Ref. 7)

In the present study, we used preparative TREF as a primary technique to separate the polyethylene into different fractions with respect to their different crystallizability and combined multiple techniques to achieve the understanding of polymer structure and property relationships.

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To our knowledge these modified TREF methods have never been studied in literature. The aim of the present work was to carry out the comparative study of the mixed solvent used in the crystallization step and to solve the problem of time-consuming.

2. Materials and Methods

Chemical composition distribution was expected to be unnarrow and unimodal. For LLDPE(1-hexene) and LLDPE(1-octene) samples, their polydispersity index (PDI) were close to 7. Table 1 summarizes the properties of the samples used in this experimental.

Table 1. LLDPE Sample Data

Sample	Co-monomer	Density ₃ (g/cm ³)	M _n	PDI
A	1-butene	0.918	29,184	3.53
B	1-hexene	-	11,507	6.61
C	1-octene	-	8,052	6.41

Experimental

Temperature rising elution fractionation (TREF)

TREF analysis was carried out with the home-made preparative TREF apparatus. The preparative TREF was proceeded by a process of crystallization which involved the dissolution of polyethylene about 1 g with o-xylene, stabilized with Irganox 1010 which was previously stirred for 1 hour at 120 °C. Pouring into the column which loaded via glass bead (24.0 g) preheated at 120 °C and cooled down to 20 °C at a constant rate of 1, 5 and 10 °C/h respectively. The column was heated incremental step and eluted with o-xylene. At each step, the elution temperature slowly increased for a period of 1 hour and then remained constant for several hours until the peak of the specimen disappeared in the refractive index detector. The polymers of each fraction were precipitated with the addition of an excess volume of methanol or acetone while stirring. Filtered, dried at 80 °C over a period of 6 h and weighed.

In the modified TREF, the mixed solvent used were polyethylene glycol (PEG) and o-xylene stabilized with Irganox 1010.

Gel permeation chromatography (GPC)

Three ethylene/ α -olefins copolymers, A B and C were used in this investigation. All samples were produced with multiple site catalysts; therefore, Chemical composition distribution was expected to be unnarrow and unimodal. For LLDPE(1-hexene) and LLDPE(1-octene) samples, their polydispersity index (PDI) were close to 7. Table 1 summarizes the properties of the samples used Water 150 °C, high temperature size exclusion chromatography, used to determine the molecular weight and with three linear mixed Shodex AT-806MS columns and a differential refractive index detector at 135 °C. The 1,2,4-trichlorobenzene (TCB) was used as the solvent at a flow rate of 1.0 ml/min. The universal calibration was carried out using monodisperse polystyrene standards.

Differential scanning calorimeter (DSC)

Melting endotherms and of whole polymers and their fractions were determined using a METTLER. The samples were heated from 50 to 200 °C at 10 °C/min. To take into account the thermal history of the samples used for the melting point and crystallinity were estimated.

¹³C-Nuclear magnetic resonance (¹³C-NMR)

This study use ¹³C-NMR to characterize whole polymers and their fractions. Spectra were obtained with a Bruker AC 300 pulsed NMR spectrometer in TCB/deuterated o-dichlorobenzene at 120 °C and were used for the determination of copolymer compositions. The acquisition parameters and procedure, the chemical shift assignments of polymer chains and the calculations of copolymer compositions followed ASTM D 5017-91 method [9].

3. Results and Discussion

Fractionation

The copolymers sample used in preparative TREF have relatively data. A comparison of the corresponding molecular weight distributions is shown in Fig. 2. The MWDs of the three resins are quite similar. The number average molecular weights (M_n) of these samples are listed in Table 1. However their polydispersity (PD) indices do vary due to short chain branching in the high molecular weight region.

The compositional distribution of the whole polymer is expressed in one way; the short chain branching content obtained from the preparative

TREF profile by combining nuclear magnetic resonance and differential scanning calorimeter. Seven fractions for LLDPE(1-butene) were collected by TREF as show in Fig. 7. Their relative weight fractions were determined using the GPC technique. Fig. 4 give the DSC thermogram on heating curve of each whole resins. Fig. 5 give the DSC thermogram on heating curve of each fraction of LLDPE(1-butene) when used the single solvent in the crystallization step. Fig. 6 give the DSC thermogram on heating curve of each fraction of LLDPE(1-butene) when used the mixed solvent. From the both figure showed that the fractionation are not different significantly. On the other hand the rate of crystallization are different. As preparative TREF elution temperature increased, the melting peak became sharper and the melting curve shifted toward high temperature. These results indicate that the increase in short chain branching content considerably diminished the melting temperature. Thus the short chain branching content is a dominant factor affecting the lamellar morphology and hence the melting and crystallization behaviors of ethylene/ α -olefin copolymers. Hence this study focuses on the effects of compositional structure on the melting and crystallization behavior.

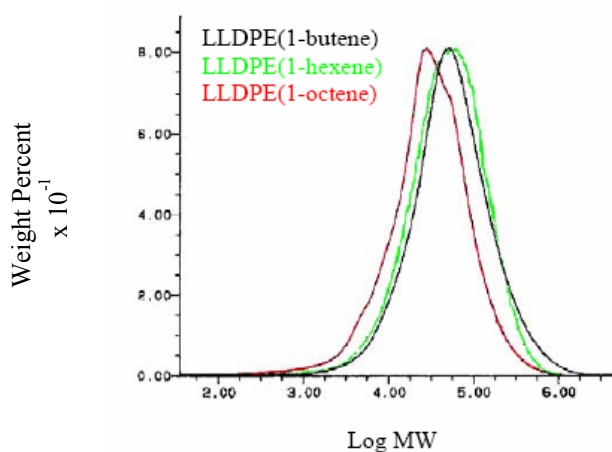


Fig. 2: Comparison of MWDs of each LLDPEs

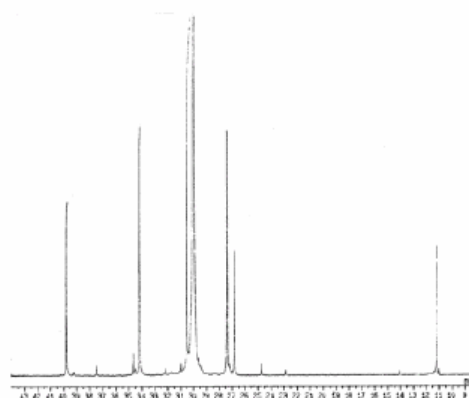


Fig. 3: ^{13}C -NMR spectrum of ethylene/butene-1 copolymers (whole resins)

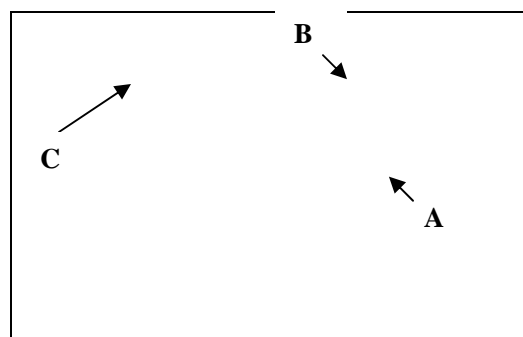


Fig. 4: DSC thermogram of each resins

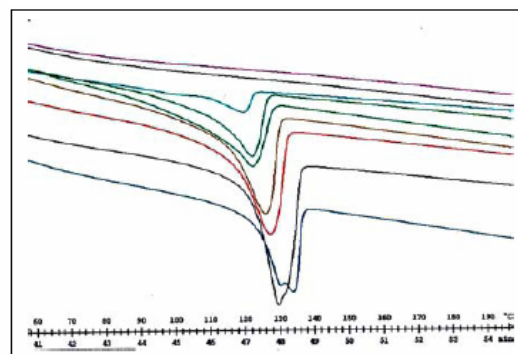


Fig. 5: DSC thermogram of each fraction of Sample A (single solvent)

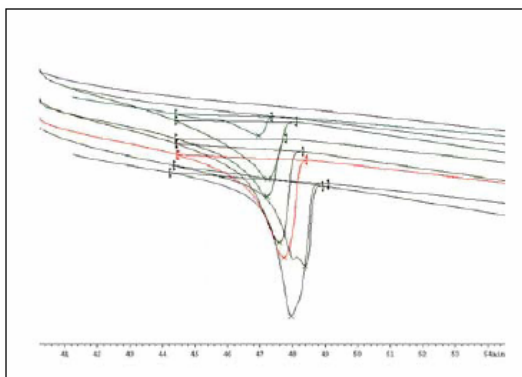


Fig. 6: DSC thermogram of each fraction of Sample A (mixed solvent)

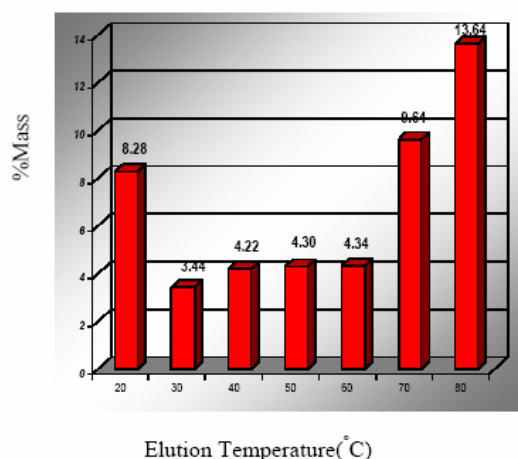


Fig. 7: Chemical composition distribution profile of LLDPE(1-butene)

4. Conclusion

From the result of this study, it found that the polarity of eluent resulted in the crystallization of polymer. Thus TREF known as a time consuming technique was improved by using mixed solvent. Therefore, the fractionation of polyethylene was significantly separated. Moreover, the modified TREF of this study not only worked potentially but saved great cost as well.

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