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Improved Temperature Rising Elution Fractionation Method for the Study of Structural Distribution in Ethylene-α-olefin Copolymer

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An improved method for the study of short-chain branching distributions in polyethylenes, on basis of temperature rising elution fractionation technique, has been developed by utilizing a chromatographic system incorporating a Fourier transform infrared spectrometer and a thermostat which is capable of regulating the column temperature in the range from -40 to 170°C. The workings of the system was under control of a central processing unit. Accuracy of the Fourier transform infrared detection method was substantiated by a gravimetric method, and the optimum experimental conditions for the temperature rising elution fractionation have been established. By applying Nishikida's method to calculate the short-chain branching from the infrared absorption in the region 3000-2760cm^{-1}, an equation, SCB/1000C=$59.67-0.599 \times T_E$, was derived, where SCB/1000C and T_E are short-chain branching per 1000 carbon atoms and elution temperature(°C), respectively. The short-chain branching distributions in polyethylenes, including ethylene-α-olefin copolymer, have been effectively performed by the present method.

KEY WORDS: Polyethylene/Ethylene-α-olefin copolymer/Short-chain branching/Crystalizability fractionation

INTRODUCTION

Cross fractionation technique, based on molecular weight distribution (MWD) and short-chain branching (SCB) distribution, is becoming extremely important for characterizing semicrystalline polymers.[1] As to MWD, gel permiation chromatography (GPC) has been much utilized for characterizing a large number of polymers including commercial products. As to SCB, Wild and Ryle developed a temperature rising elution fractionation (TREF) technique, for crystalizability fractionation, to study SCB in semicrystalline polymers.[2] Nakano and Goto published an automatic cross fractionation system, by combining a crystallizability fractionation device based on the principle of TREF with a commercially available GPC[3] and applied their system to a low density polyethylene (LDPE) and a high density polyethylene (HDPE).

The TREF systems so far reported[4], however, indicate necessity of TREF runs to be extended down below room temperature, when polymer species with lower crystalizability are not negligible.

We have developed a multifunctional column liquid chromatograph (MCLC), with a thermostat built in to regulate column temperature down to -40°C, coupled with an

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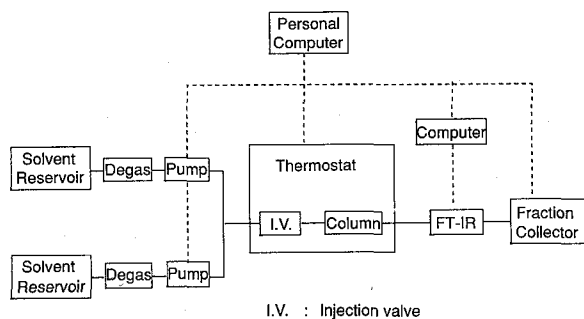2-1 Kitasode, Sodegaura, Chiba 299-02

Fig. 1　Schematic diagram of the experimental system (MCLC)

Fourier transform infrared spectrometer (FTIR) as a detector. In this paper, we describe an improved TREF method for the study of structural distribution in ethylene-α-olefin copolymer, by utilizing MCLC.

EXPERIMENTAL

Instrumentation

A schematic diagram of the MCLC is shown in Fig. 1. The system consisted of two solvent reservoirs, a degassing unit (model ERC-3322; Erma), two double-plunger pumps (model CCPM;Tosoh), a thermostat (model SSP-43CR-A; Kato) which houses an injection valve (model M3-1/16-V6-P-SS; Valco) and a stainless steel column unit (serectively replaceable for TREF, GPC and LC), FTIR (model 1720X; Perkin-Elmer) and a fraction collector (model MV-8010-k; Tosoh) with 16-port valve. A polytetra-fluoroethylene tubing (1.5mm i.d., 1.0mm wall thickness) and a stainless steel tubing (0.5mm i.d., 0.55mm wall thickness) were used as a conduit from reservoir to pump and from pump to fraction collector, respectively. The thermostat is capable of regulating the chamber temperatures programmed in the range from -40 to 170°C, within difference of 2.0°C and 0.2°C at -5°C and 100°C, respectively. A heater-jacketed conduit was used from the thermostat to the fraction collector. For purpose of large amount of sample preparation, a large size column (30mm i.d.×500mm) was used.

The workings of the pumps, the thermostat, the FTIR and the fraction collector are controlled by a personal computer (model SC-8010;Tosoh).

Procedure

Outline of the standard procedure for TREF is shown in Table 1. A polymer solution is injected into the sample loop by a syringe. Then, a constant volume of the solution in the sample loop is introduced into the column by turning the injection valve manually to the position(2) in which the sample loop is placed in a line to the column. When the sample solution is carried to the middle part of the column, the injection valve is turned to the original position(1). The temperature is then decreased from 145°C down to low enough so that the polymer species are precipitated completely on the support. The polymer species precipitated on the support are stepwise disolved

Table 1   Standard Procedure for TREF

Step	Practice	Experimental conditions
1	Sample preparation (polymer solution)	Concentration; 1% in o-dichlorobenzene, Heated at 145°C for 4h
2	Injection	Sample volume; 6ml
3	Polymer precipitation	Column size; 21mm i.d.×150mm (18ml) Support; 70g of sea sand (50 mesh through/ 80 mesh on), Cooling; refer to condition 2 in Fig. 3
4	Polymer dissolution	Elution temp. range; 0 to 125°C (22 steps) Solvent volume; 62.5ml/fraction Flow rate for elution: 2.5ml/min

Table 2   Characteristics of Samples

Sample	Type of polyethylene	Comonomer		SCB[a] (1/1000C)	Mw (g/mol)
		α-olefin	Content		
A	LLDPE	butene-1	6.7	31.6	12.4×10^4
B	LLDPE	hexene-1	4.3	20.0	11.1×10^4
C	LLDPE	butene-1	3.2	15.3	13.4×10^4
D	HP-LDPE	—	—	10.0	8.1×10^4
E	HDPE	—	—	1.5	6.4×10^4

a) Ref. 7

in a constant volume of solvent by stepwise increment of temperature. The solution in the column, then, is carried to the fraction collector through a flow cell in the FTIR, by turning the injection valve to the position(2) when single stepwise increment of temperature is completed. This procedure is repeated 22 times for linear low density polyethylene (LLDPE), resulting in 22 fractions.

Samples

The characteristics of the samples used in the present work are listed in the Table 2. High-pressure low density polyethylene (HP-LDPE) and HDPE are included.

RESULTS AND DISCUSSION

FTIR Detection Method

A conventional IR detection method has been utilized semi-quantitatively for TREF experiments.[4,5] In the present work, however, the species eluting from the column are detected with the FTIR set at the wave number region 3000-2760cm^{-1}[1] (absorption due to methyl and methylene groups). In order to examine the quantitative accuracy of the FTIR detection method by a gravimetric one, the polymer species eluted from the large size column were precipitated in methanol, separated and
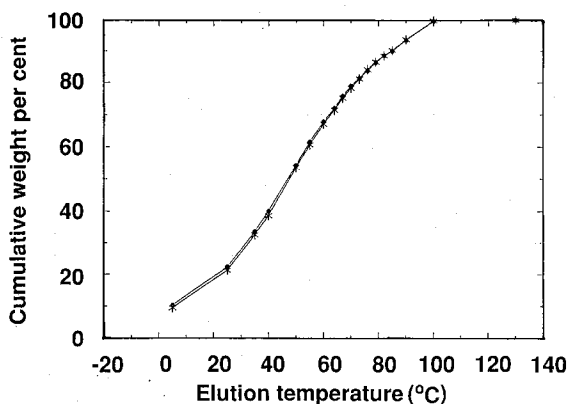
Fig. 2   Plot of cumulative weight per cent *vs.* elution temperature with FTIR detection (●) and methanol precipitation(*): sample; A, sample weight; 3g, column size; 30mm id.×500mm, IR detection; 3000–2760cm⁻¹.

weighed. Cumulative curves obtained by the both were compared in Fig. 2 (one hundred per cent in the ordinate represents the sum total of all fractions). This indicates that the quantitative accuracy of the FTIR detection method was substantiated by a gravimetric method. It was also calculated that the recovery for the original solid sample through the whole process was 97.0 per cent.

Cooling Rate for Polymer Precipitation

Polymer solution injected from the sample loop to the column was cooled from 145°C at four different rates, A, 1, 2 and 3, as shown in Fig. 3, and dependency of the cumulative weight percent vs. elution temperature curve on cooling rates was examined. Figure 4 shows the cumulative TREF curves obtained for four different cooling conditions. The area under the curve become larger in order of 3, 2, 1, and A, but not so much difference in the later three conditions. The condition 2, i.e. (from 145 to 90°C)/1h, (from 90 to 0°C)/6h, and 2h at 0°C) was chosen as the standard cooling condition.

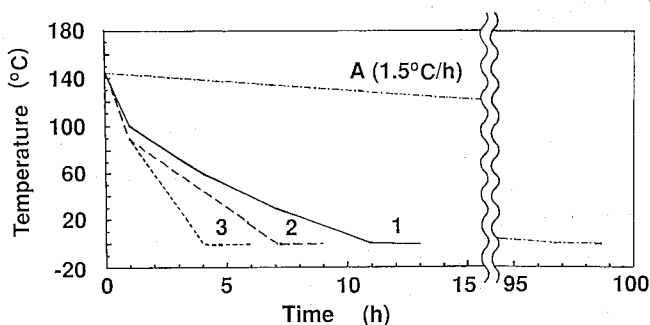**Polymer Concentration vs. Elution Time**
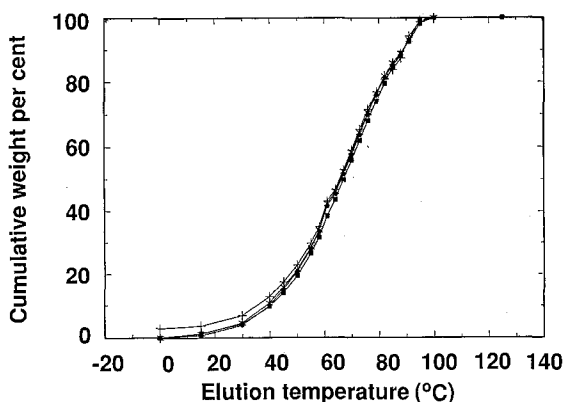

Fig. 3   Cooling curves

Fig. 4   Dependency of cumulative TREF curve on coo-
ling conditions: symbols ■, ●, ∗ and + corre-
spond to the cooling conditions A, 1, 2 and 3 in
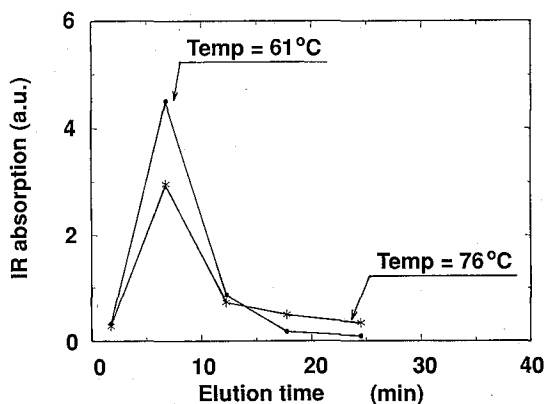Fig. 3, resepectively. Sample; B.

Fig. 5   Polymer concentration $vs.$ elution time: sample;
B.

The polymer species precipitated on the support are dissolved in the column in
accordance with stepwise increment of temperature. The solution in the column is
transferred to the fraction collector with certain volume of carrier solvent, resulting
in single fraction in the process of TREF. In order to determine the necessary and
minimum volume of carrier per a fraction, IR absorption (peak area in the region 3000
$-2760cm^{-1}$ is recorded as a function of elution time, as shown in Fig. 5. Eluting polymer
concentration becomes maximum around 7 min, and practically negligible around 25
min. As the carrier flow rate was set at 2.5ml/min, the necessary and minimum volume
of carrier was determined as 62.5ml which corresponds to 3.6 times of the volume in
the packed column.

SCB Determination of Fractionated Polymer

Infrared spectrum for each fraction can be obtained on real time by means of the
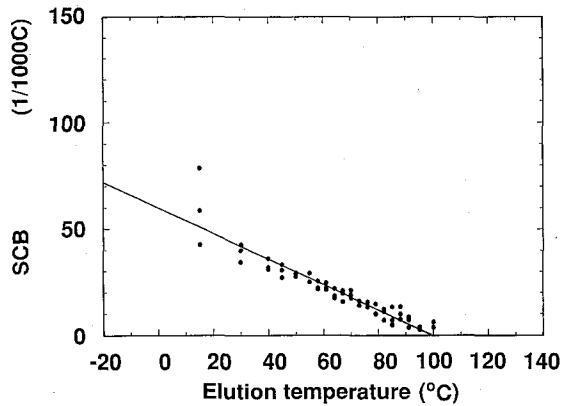FTIR detection system incorporated in the flow line. According to Nishikida's

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Fig. 6   Relation between degree of SCB and elution
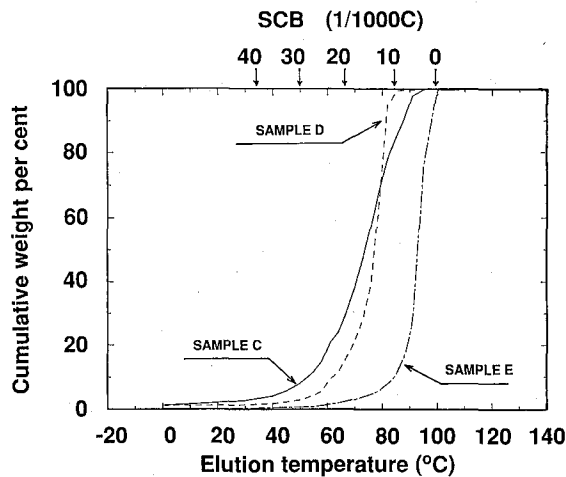temperature: sample; B.

Fig. 7   SCB distribution in polyethylenes

method[6], SCB is caluculated from the IR spectrum in the region 3000-2760cm^{-1} where
two peaks due to methyl and methylene groups overlap. After resolving the overlapped
peaks into two ones with wave numbers of 2955 (symmetric stretching vibration of
methyl) and 2928 (antisymmmertic stretching vibration of methylene)cm^{-1}, SCB is
figured out from the ratio of (methyl peak area)/(methylene peak area), by using a
calibration curve. Figure 6 shows the relation between SCB and elution temperature
(T_E) of the fractions. It is seen that there is a linear relation between SCB and T_E
according to the equation

$$SCB/1000C = 59.67 - 0.599 \times T_E \tag{1}$$

where SCB/1000C is the short-chain branching or methyl groups per 1000 carbon atoms
in the polymer chain.

SCB Distributon in Polyethylenes

Fractionation of three types of polyethylenes was done by the present TREF method. The distribution of SCB for each sample is shown in a form of cumulative curve in Fig. 7. It is clearly seen that sample C exibits extremely broad distribution over wide range of SCB, but samples D and E possess rather sharp distributions in the range between 10 and 20 SCB, and 0 and 5 SCB, respectively.

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