

Title	ストップフロー法によるポリプロピレン系コポリマーの合成と結晶性分布の評価
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Crystallinity Distribution of Propylene-block-Poly(Ethylene-co-Propylene) Prepared by Stopped-flow Polymerization Method

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Introduction

The commercial polypropylene (PP) can be usually divided roughly into three grades according to the structure and composition: homopolymer, random copolymer, and block-type copolymer, that is impact copolymer (ICP). In particular, ICP has improved toughness and therefore applied for the various industrial fields such as electronic and automobile fields. ICP is generally produced by two-stage polymerization process with MgCl_2 -supported Ziegler catalyst in which homopolymer and poly(ethylene-co-propylene) (EPC) are sequentially produced^{1)–5)}. At first, polymerization of propylene is carried out in the first series of reactors (1~several hours). Then, copolymerization of ethylene and propylene is carried out in the second series of reactors. However, most of EPC chains are not connected to a homopolymer chain through a covalent bond because chain transfer reactions are so frequently occurred. ICP is eventually a blend of PP, polyethylene (PE), and EPC. For further improvement of PP materials, it is desired to develop real block copolymer in which a homopolymer chain and an EPC chain are connected through a covalent bond.

It has been reported that in a stopped-flow polymerization method, the chain transfer reactions are nearly negligible because of its very short polymerization period below 0.2 s^{6), 7)}. Therefore, it was expected to be able to connect PP and EPC by the method. In this study, three-vessel (two-stage) stopped-flow polymerization was conducted to make propylene-block-poly(ethylene-co-propylene) (PP-block-EPC). It was confirmed that the obtained PP-block-EPC was a real block type, based on its crystalline distribution. Furthermore, the EPC part of PP-block-EPC was separately characterized from the PP part.

Experimental

Catalyst preparation

MgCl_2 (36 g) and ethyl benzoate (7.8 ml) were placed in a 1 L stainless steel vibration mill pot with 55 stainless balls (25 mm diameter) under nitrogen and co-ground for 30 hours at RT. The ground product was vigorously stirred with TiCl_4 (400 ml) in a 1 L

flask at 90°C for 2 hours under nitrogen. The reaction product was washed with 200 ml of *n*-heptane 3 times at 70°C, 5 times at 50°C, and once at RT. The catalyst was then washed with 200 ml of toluene 3 times and stored as toluene slurry. A small amount of the catalyst slurry was dried to determine the concentration (90 mg/ml). The Ti content was measured by titration with the aqueous solution of sulfateferric ammonium and sulfuric acid in the presence of solution of thiocyanate ammonium as an indicator (1.97 wt%).

Synthesis of PP-block-EPC

The apparatus used in this study is schematically illustrated in Fig.1. Vessels (A), (B), and (C) are 150 ml vessels equipped with stirrers and water jackets. The measured amount of the catalyst in toluene (0.47 mmol-Ti in 100 ml), toluene solution of TIBA (14 mmol in 100 ml), and toluene (100 ml) were placed in vessels (A), (B), and (C), respectively. The Al/Ti molar ratio was kept at 30.

Propylene was introduced at normal pressure into vessels (A) and (B) for 15 min at 30°C to saturate toluene in them. Toluene in vessel (C) was saturated with ethylene similarly. Toluene was used as a solvent because of the higher solubility of ethylene than in heptane. (D) is a 500 ml beaker containing conc. HCl (20 ml) and ethanol (200 ml) with a vigorous agitation for quenching polymerization immediately. The contents of the vessels were flown through Teflon tubes to conduct polymerization. Propylene polymerization was occurred during point (a) to (b), followed by copolymerization with ethylene and propylene during point (b) to (c). Polymerization time of propylene was set to 0.1 s and copolymerization time to 0.05 s. The inner diameter of the Teflon tubes was 2.0 mm except the part of 2.5 mm diameter between point (b) and (c). Polymerization time was precisely adjusted by changing the length of the corresponding part. The obtained polymer was washed with water and dried. Then, the polymer was dissolved into a small amount of xylene and poured into the mixture of ethanol (400 ml) and water (100 ml).

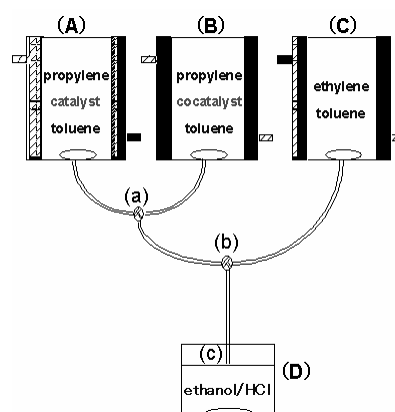


Fig.1. Three-vessel stopped-flow polymerization apparatus

Then, the apparatus in Fig. 2 was constructed to remove the catalyst residue from the polymer. In this method, the polymer on a glass filter was washed for 10 hours by *n*-heptane which was evaporated from flask and then cooled by water. Finally, the product was dried in vacuo at 60°C for 6 hours.

Synthesis of homo PP

Homo PP was polymerized by two-vessel stopped-flow method. Where the apparatus was similar to that in Fig.1. The polymerization time

of propylene was set to 0.1 s. The obtained homopolymer was washed similarly to the PP-block-EPC except that the catalyst residue was removed by reprecipitation from a boiling xylene to methanol.

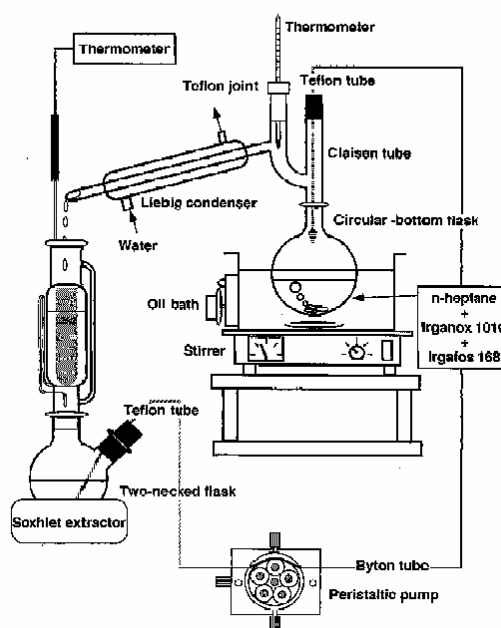


Fig.2. Special apparatus to remove the catalyst residue.

Analysis

The molecular weight and molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC, Waters Associates, ALC/GPC 150C) with polystyrene columns (Showa Denko K. K., AD806M/S) at 140°C using *o*-dichlorobenzene (containing 2,6-di-*tert*-butyl-4-methylphenol) as solvent.

The isotacticity of the polymer was determined by ¹³C NMR spectroscopy (Varian Instruments Ltd. Gemini-300 spectrometer at 120°C). The polymer was dissolved in 1,1,2,2-tetrachloroethane with hexachloro-1,3-butadiene as an internal standard.

The crystallinity distribution of the polymer was measured and fractionated on the basis of crystallinity by temperature raising elution fractionation (TREF, Senshu Scientific Co., Ltd. SSC-7300). The polymer was dissolved in *o*-dichlorobenzene (containing 2,6-di-*tert*-butyl-4-methylphenol). The original polymer was fractionated in three in different temperature regions: RT~35°C, 35~80°C and 80~160°C.

Results and discussion

The crystallinity distribution of the obtained polymer was investigated by TREF (Fig.3.).

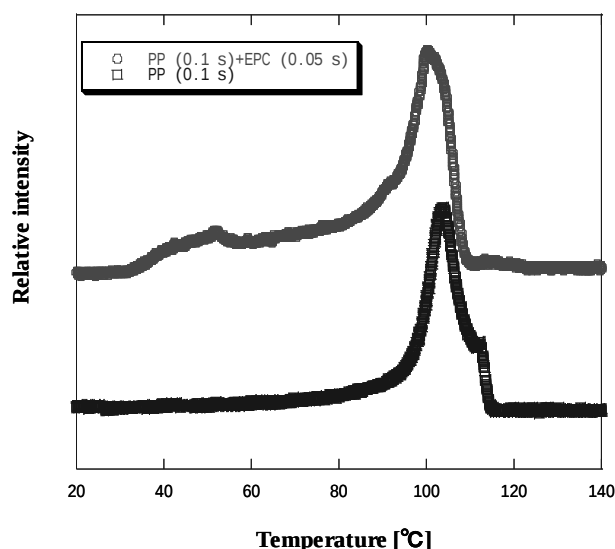


Fig 3. Crystallinity distribution of homo PP and PP+EPC

When PP and EPC synthesized separately are blended, the whole EPC is eluted below 20°C without changing the crystallinity distribution of the PP. However, the PP-block-EPC synthesized with three-vessel stopped-flow polymerization method showed the shift of the crystallinity distribution of the PP to the low temperature side, which proved that the obtained PP-block-EPC was a real block type.

In order to understand the relation between the shift on the crystallinity distribution and ethylene content in PP-block-EPC, the PP and PP-block-EPC were fractionated into three: fraction 1 (RT~35°C), fraction 2 (35~80°C) and fraction 3 (80~160°C). Table 1 shows the weight ratio and ^{13}C NMR results of each fraction. At first, the weight ratio of fraction 3 significantly decreased (almost 50%) by adding the EPC part, i.e. the addition of EPC lowered the degree of crystallinity. This was supported by the fact the ethylene content of fraction 3 for the PP-block-EPC was the smallest.

Table 1. Results of fractionation by TREF

sample	wt%	ethylene content [%]	mmmm [mol%]
PP-block-EPC (Original)	100	31.6	69.2
fraction 1	39	36.5	62.1
fraction 2	18	45.2	60.7
fraction 3	43	22.1	76.8
PP (0.1 s) (Original)	100	-	94.5
fraction 1	8	-	70.0
fraction 2	8	-	85.8
fraction 3	84	-	96.0

The characteristics of the obtained real block copolymer and PP were shown in Table 2. The characterization of the EPC part could be approximately determined based on the molecular weights and polymerization degrees of the PP synthesized by two-vessel stopped-flow polymerization method and PP-block-EPC, and the ethylene content of the PP-block-EPC.

Table 2. Characteristics of PP and PP-block-EPC

sample	polymerization time [s]		$\overline{M}_n$	yield [g/mol-Ti]	n_{total}	mmmm [%]	ethylene content [%]
	PP	EPC					
PP-block-EPC	0.10	0.05	16655	198	458.6	69.2	31.6
PP	0.10	-	8470	101	201.6	94.5	-
EPC*	-	0.05	8185	97	257.0	-	56.3

* The characteristics of the EPC part in the PP-block-EPC was determined by subtracting the contribution PP from the PP-block-EPC.

In this way, the characteristics of EPC part in the PP-block-EPC were analyzed (Table 3). The calculated ethylene content of the EPC part was as high as 56.3 mol%. The average chain lengths of propylene and ethylene monomer units were 2.81 and 3.63, respectively. And the χ value as an indicator of the copolymerization pattern was 0.72, i.e. the EPC part was a random copolymer with a little blocky nature. k_{XY} is the propagation rate for Y when the end of growing polymer is X. It was understood that the propagation rates of each monomer were faster when the chain end was the same monomer: $k_{PP} > k_{EP}$ and $k_{EE} > k_{PE}$. The propagation rate constant of ethylene, the k_E is 7 times higher than the k_P .

sample	polymerization time [s]	$\overline{Mn}$	ethylene content [%]	L^*_P	L^*_E	χ
EPC	0.05	8185	56.3	2.81	3.63	0.72
	k_{PP} [l/mol·s]	k_{PE} [l/mol·s]	k_{EE} [l/mol·s]	k_{EP} [l/mol·s]	k_P [l/mol·s]	k_E [l/mol·s]
	5520	16320	33290	2360	3730	25880

Table 3. Characteristics of the EPC part

* Average chain length

From these result, it was understood that synthesis of PP-block-EPC was succeeded and high crystallinity part was easily shifted to low crystallinity by adding the EPC part.

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