DOI: 10.1002/masy.200751110

Application of Fractionation Techniques to the Study of Olefin Polymerization Kinetics and Polymer Degradation

Hisayuki Nakatani,[1] Hitoshi Matsuoka,[2] Shoutarou Suzuki,[3] Toshiaki Taniike,[3] Liu Boping,[3] Minoru Terano[3]*

Summary: Temperature rising elution fractionation (TREF) has been regarded as a powerful technique for study of semicrystalline polymers. In this paper, two examples of unique applications of TREF were introduced. One was the study on the influence of extraction of internal donor on the variation of isospecific active sites of a $MgCl_2$-supported Ziegler catalyst, and the other was the estimation of the relationship between polymer micro-tacticity and degradation rate of isotactic polypropylene (iPP). The former example revealed the conversion from high to low isospecific site by the extraction of internal donors, whereas the latter showed a negative correlation between the level of isotacticity and the degradation rate. These results demonstrated that TREF was useful in these research applications.

Keywords: catalyst; degradation; fractionation polymers; isotactic; polypropylene

Introduction

Analytical TREF has been a useful technique for the quantitative structural analysis of semicrystalline polymers.[1–3] In addition, TREF is a well-known procedure to fractionate each polymer component by differences of crystallizability. TREF has been regarded as the method of choice for the analysis and fractionation of polymer crystalline distribution.

It should be noticed here that the crystallizability of isotactic polypropylene (iPP) strongly depends on its isotacticity. In the case of iPP synthesized by $MgCl_2$-supported Ziegler catalysts, the iPP obtained often shows a broad distribution of isotacticities. This distribution directly reflects the existence of various isospecific active sites on the catalyst, with individual fractions of narrow isotactic distributions being produced by each corresponding active site type. TREF application for such iPP reveals the distribution profile of isospecific active sites on the Ziegler catalyst.[4,5]

Another substantial advantage of TREF is the fractionation of iPP with broad isotacticity distribution into several fractions of different isotacticities. In our previous studies,[6,7] the effect of tacticity on thermal oxidative degradation of polypropylene was investigated using highly isotactic, syndiotactic and atactic polypropylene resins, suggesting that the degree of oxidation of iPP was the severest. On the basis of this result, it was concluded that the tacticity affects one reaction path in the degradation process. However, the relationship between the level of tacticity and the rate of degradation had not been systematically clarified. The elucidation of this phenomenon requires the use of a systematic iPP series

---

[1] Kitami Institute of Technology, Koen-cho, Kitami, Hokkaido, 090-8507, Japan
[2] Tsukuba Research Laboratories, Tokuyama Corporation, 40, Wadai, Tsukuba-shi, Ibaraki, 300-4247, Japan
[3] Japan Advanced Institute of Science & Technology, Nomi, Ishikawa, 923-1292, Japan
Fax: (+51)761511625
E-mail: terano@jaist.ac.jp

with various isotacticities. By development of polymerization catalyst technology in recent years,[8–10] it is possible to control the tacticity of polypropylene. However, it is difficult to directly synthesize an iPP series with different isotacticities with only one kind of catalyst. The study of the relationship between degradation characteristics and isotacticity of iPP requires an iPP series with systematic isotacticity variation, and it has been difficult to synthetically supply such iPP series in practice. A better method is to fractionate a single iPP resin having broad isotacticity distribution witeh TREF to generate such a iPP series with various isotacticities.

In this paper, two kinds of TREF applications are reported: one to evaluate the influence of extraction of internal donor on the change of isospecificity distribution on $MgCl_2$-supported Ziegler catalysts and the other to clarify the relationship between the level of tacticity and the rate of degradation of iPP.

Experimental Part

Materials

Research grade propylene, donated by Tokuyama Corp., was used without further purification. $MgCl_2$ was kindly supplied by Toho Titanium Co., Ltd.

Propylene of research grade (donated by Tokuyama Corp and Chisso Corp.), anhydrous $MgCl_2$, $TiCl_4$, $TiCl_3$ (donated by Toho Catalyst Co.), nitrogen (purchased from Uno Sanso Co.), and triethylaluminum (TEA) (donated by Tosoh Finechem Co.) were used without further purification. Heptane, toluene, ethylbenzoate (EB) and dibutylphthalate (DBP) were purified by passage through a 13X molecular sieves column. TEA, EB and DBP were used as toluene solution.

Catalyst Preparation

Two types (Cat-A and Cat-B) of $TiCl_4$/$MgCl_2$ catalysts with two types of internal donors and one type of $TiCl_3$/$MgCl_2$ catalyst without any donors were prepared as follows.

Cat-A: $MgCl_2$ (36 g; 11 m^2/g), and EB (7.2 ml) were placed in a 1.2 L stainless steel vibration mill pot with 55 balls (25 mm diameter) under nitrogen and ground for 30h at room temperature. The ground product (200 ml) was treated with $TiCl_4$ (200 ml) in a 1.0 L three-necked flask at 90 °C for 2h with stirring under nitrogen, followed by washing several times with heptane and finally stored as a toluene slurry before polymerization. The Ti content of the catalyst was found to be 0.46 mmol-Ti/g-cat.

Cat-B: Cat-B was prepared by the same procedure as Cat-A, with DBP (7.2 ml) instead of EB. The Ti content of the catalyst was found to be 0.50 mmol-Ti/g-cat.

$TiCl_3$/$MgCl_2$: $TiCl_3$/$MgCl_2$ catalyst was prepared by grinding $MgCl_2$ and $TiCl_3$ in a 1.2 L stainless steel vibration mill pot with 55 balls (25 mm diameter) under nitrogen atmosphere for 30 h at room temperature. The Ti content of catalyst was 0.05 mmol-Ti/g-cat.

Extraction of Internal Donor

The $MgCl_2$ supported catalyst (about 1 g), TEA (14 mmol, Al/Ti mole ratio = 30) and toluene (200 ml) were placed in a 300 ml flask under nitrogen and the mixture was stirred at 30 °C for a selected time (from 1 to 30 min). The resulting catalyst was then recovered by filtration.

Propylene Polymerization and Estimation of Kinetic Parameters by Stopped-Flow Method

Stopped-flow polymerization of propylene and estimation of the kinetic parameters were carried out according to a previously reported method.[11–13] The propylene polymerization was typically performed with the catalyst (Cat-A or Cat-B: ca.1.0 g) and TEA (14 mmol, Al/Ti mole ratio = 30) in toluene at 30 °C for 0.15 s. The TEA solution in toluene (100 ml) saturated with propylene (1 atm) was placed into the vessel.

The propagation rate constant (k_p) and the concentration of active sites ($[C^*]$) were

Table 1.
Yield, molecular characterization, and kinetic data of iPP.

Catalyst	Extract. time	Int. donor cont.[a)]	Yield	$M_n(M_w/M_n)$[b)]	mmmm[c)]	k_p	[C*]
	min	wt%	g/mol-Ti		mol%	l/mol · s	mol%
Cat-A	none	9.7	130	6100(3.3)	92.0	2700	2.15
	1	1.6	108	4800(3.8)	81.2	2400	2.01
	5	0.7	85	4700(4.0)	70.3	2100	1.81
	30	0.3	71	4000(4.2)	60.4	1600	1.75
Cat-B	none	12.8	53	6600(3.2)	94.0	3000	0.79
	1	8.7	45	5400(3.6)	88.4	2650	0.77
	5	8.0	42	5200(3.8)	85.2	2500	0.75
	30	5.5	37	4700(4.2)	78.5	2300	0.72

Polym. condition: Al/Ti = 30, polym. temp. = 30°C, polym. time = 0.15s;

[a)] Amounts of remaining internal donor on catalyst after extraction experiment were determined by GC;

[b)] Molecular weight and its distribution were determined by GPC;

[c)] Meso pentad fraction was determined by ^{13}C-NMR.

determined by the following equations:

$$M_n = M_0 * \frac{k_p * [M] * t}{1 + k_{tr} * t} \qquad (1)$$

$$Y = k_p * [M] * [C*] * t \qquad (2)$$

where M_n, M_0, [M], t, k_{tr}, and Y are number-average molecular weight of polymer, molecular weight of monomer, monomer concentration, polymerization time, transfer rate constant, and polymer yield, respectively.

The iPP having broad isotacticity distribution was synthesized using $TiCl_3/MgCl_2$ catalyst and TEA. Polymerization was performed at an Al/Ti molar ratio of ca. 2 at 30 °C for 30 min in toluene. In order to remove catalyst residues, the obtained iPP was reprecipiated from a boiling xylene solution into methanol under nitrogen atmosphere.

Temperature Rising Elution Fractionation (TREF)

The isotacticity distribution of iPP polymerized with the $TiCl_3/MgCl_2$ catalyst system was determined by TREF (Senshu SSC-7300) using *o*-dichlorobenzene (ODCB) containing antioxidant (*2,6-di-t*-butyl-*p*-cresol) as the extraction solvent. A fractionation column packed with Chromosorb (Celite Corp.) with 10 mm diameter and 30 cm in length was used for the TREF characterization. About 1.4 g of iPP was dissolved in 70 ml of ODCB at 140 °C. A

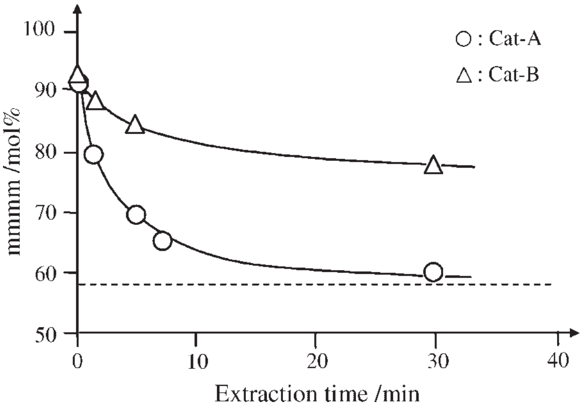

Figure 1.
Plots of extraction time versus isotacticity of iPPs obtained from Cat-A and Cat-B: Dashed line represents isotacticity of iPP obtained from no internal donor catalyst.

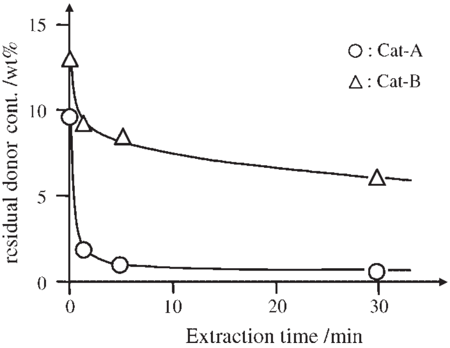

Figure 2.
Content of residual internal donor as a function of the extraction time.

part of the solution (50 ml, ca. 20 mg/ml) was eluted through the fractionation column. The column was then cooled to 20 °C slowly (6.7 °C/h). Elution with ODCB (150 ml/h) was first carried out at 20 °C for 30 min to obtain the ODCB-soluble fraction, and then the column was heated up to 140 °C at 10 °C/h.

The precise fractionation of iPP was carried out with the same TREF device, solvent, and column. About 70 mg of the iPP was dissolved in 10 ml of ODCB at 140 °C, and a part of the solution (ca. 6 ml) was passed through the fractionation column, which was slowly cooled down at 6.7 °C/h from 140 °C to 20 °C. Elution of the deposited iPP with ODCB at a flow rate of 150 ml/h was first carried out at 20 °C for 30 min to obtain the ODCB-soluble fraction, and then the column was heated at 16 °C/h up to 140 °C. The eluted iPP solution was analyzed by a refractive index detector to obtain the TREF diagram. Moreover, tacticity fractions of the iPP with increasing crystallinity were then eluted with ODCB at the temperatures increasing stepwise from 20 °C to 140 °C divided into 5 steps (20, 60, 90, 106 and 140 °C). Polymer was eluted during 90 min at every step after the temperature had stabilized for 30 min. The fraction was then collected and precipitated in methanol. All fractionated iPP were TREF fractions insoluble below 20 °C. The weight fraction of the soluble part (below 20 °C) was 52 wt%, and its molecular weight and tacticity were very low ($M_n = 6{,}000$ and mmmm = 25 mol%). Since this soluble part was considered to contain impurities, such as unsaturated polymer chain end groups, for promoting degradation,[10] it was completely removed.

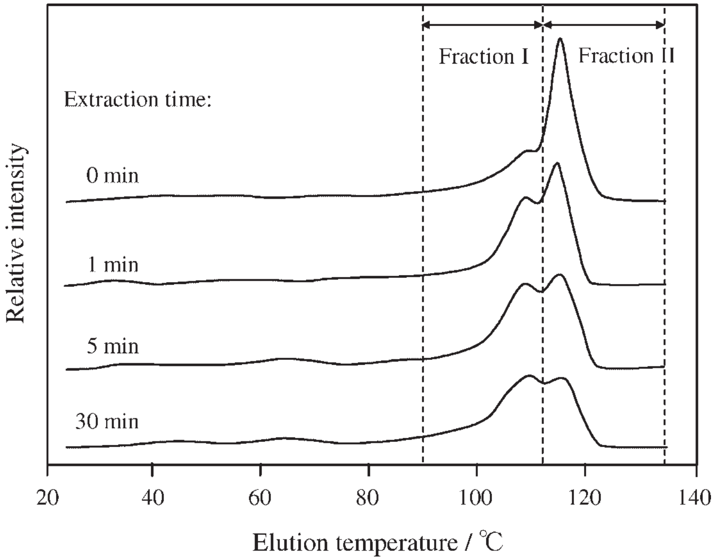

Figure 3.
TREF diagrams of iPPs obtained from the extracted Cat-A.

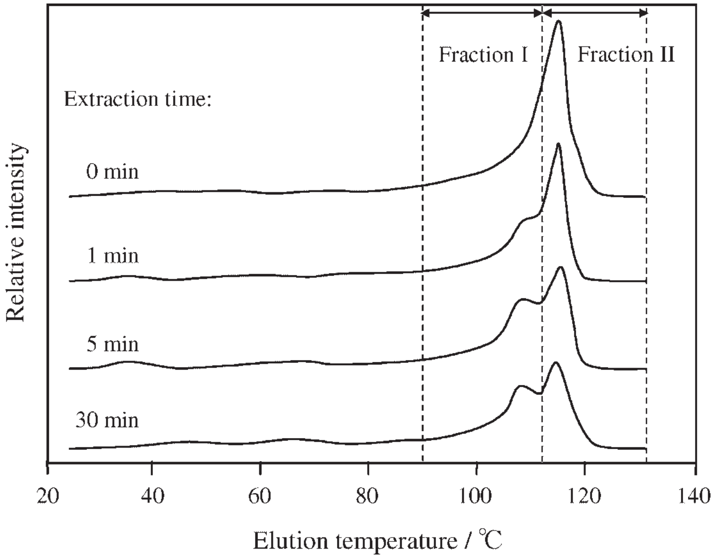

Figure 4.
TREF diagrams of iPPs obtained from the extracted Cat-B.

GPC Characterization

The sample in the small vial was dissolved in 5ml of ODCB containing 2,6-di-t-butyl-p-cresol as an antioxidant, and the obtained solution was directly measured by GPC. The molecular weight was determined by GPC (Senshu, SSC-7100) with styrene-divinylbenzene gel columns (SHODEX, HT-806M) at 140 °C using ODCB as a solvent.

^{13}C-NMR Measurement

Isotacticity was determined by ^{13}C-NMR measurement using a Varian Gemini-300 spectrometer at 120 °C on 20 % (w/v) solution in 1,2,4-trichlorobenzene or hexachloro-1,3-butadiene. Benzene-d_6 or 1,1,2,2-tetrachloroethane-d_2 was added as an internal lock and was used as an internal chemical shift reference.

Thermal Oxidative Degradation

Thermal oxidative degradation of the fractionated iPP was performed at 130 °C for 10–120 min in air using a Senshu SSC-9300 heater. No additional antioxidant was used in any cases. The iPP sample was first dried

Table 2.
Characterization and kinetic data of Fraction I and Fraction II in the iPP obtained from extracted Cat-A catalyst*.

Fraction	Extract. time	M_n	mmmm	k_p	[C*]
	min		mol%	l/mol · s	mol%
Fraction I	0	10 500	95.0	4700	10
	1	10 500	94.7	4700	13
	5	11 000	94.3	4900	18
	30	10 500	94.5	4700	24
Fraction II	0	27 800	98.6	12 500	40
	1	27 600	98.2	12 300	36
	5	28 000	98.4	12 500	30
	30	27 400	98.5	12 200	16

[b] *Polymerization condition and analytical methods are the same as Table 1.

Table 3.
Characterization and kinetic data of Fraction I and Fraction II in the iPP obtained from extracted Cat-B catalyst*.

Fraction	Extract. time	M_n	mmmm	k_p	[C*]
	min		mol%	l/mol · s	mol%
Fraction I	0	10 600	95.2	4800	8
	1	10 700	95.1	4900	9
	5	10 500	95.4	4700	11
	30	10 500	94.8	4700	14
Fraction II	0	27 500	98.5	12 300	22
	1	27 400	98.5	12 200	19
	5	27 300	98.6	12 200	15
	30	27 600	98.7	12 300	10

[a] *Polymerization condition and analytical methods are the same as Table 1.

in vacuo at 60 °C for 3 h. Then, 5 mg of each iPP sample placed in a small vial was transfer to the heater and covered with a heating jacket to achieve effective heat transfer to the iPP sample.

Thermogravimetric Analysis

Decrease in weight of iPP was analyzed by thermogravimetric analysis (TGA, METTER TG50) at 130 °C for 40 h under air (air flow rate: 50ml/min.).

Results and Discussion

TREF Application for Polymerization Kinetics

Polypropylene was prepared by the stopped-flow method. It is noticed here that this method applies very short polymerization times in which chain transfer reactions can be disregarded to simplify Equation (1).[11] Characterization and kinetic data of the obtained iPPs were summarized in Table 1. All yields and M_n decrease with the treatment time by TEA, suggesting that the extraction of internal donor critically affects the concentration of active sites ([C*]) and k_p in $TiCl_4/MgCl_2$ catalyst systems.

Figure 1 plots extraction time versus isotacticity. The isotacticity decreases with increasing extraction time. It seems that Cat-A and Cat–B loose their isospecific active sites in the extraction process. In the case of the $TiCl_4/MgCl_2$ catalyst without internal donor, the isotacticity (mmmm) was almost 58 mol% under the same polymerization conditions (see the dashed line in Figure 1). As shown in the figure, the isospecificity of Cat-A rapidly reaches that of the catalyst without internal donor, indicating that the interaction between active sites and EB is weaker than that between active sites and DBP.

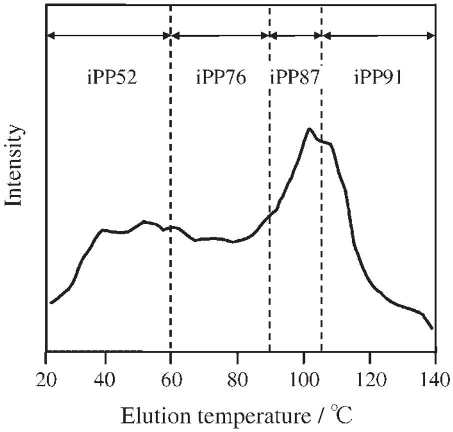

Figure 5.
TREF diagram of iPP with broad isotacticity distribution.

The content of the residual internal donor as a function of extraction time is shown in Figure 2. Here the contents of these residual donors were determined by gas chromatography. EB was extracted rapidly from the catalysts. The extraction rate of EB is higher than that of DBP, demonstrating that the interaction between EB and $MgCl_2$ is weaker. It is noticed here that this rapid change is apparently different from the rather slow one for isospecificity. Although donor extraction certainly causes a decrease in the number of isospecific active sites, it can not account

Table 4.
Fraction ratio and molecular weight of fractionated iPPs.*

Sample	Range of elut. temp. /°C	Fraction ratio /wt%	M_n	M_w/M_n
—	20	52	0.6 × 104	—
iPP52	20–60	17	1.1 × 104	4.6
iPP76	60–90	12	1.8 × 104	5.1
iPP87	90–106	9	2.5 × 104	3.2
iPP91	106–140	10	7.4 × 104	8.5

[b] *Analytical method is the same as Table 1.

Table 5.
^{13}C-NMR pentad distribution (mol%) for iPPs.

Samples	mmmm	mmmr	rmmr	mmrr	mmrm+rrmr	mrmr	rrrr	mrrr	mrrm
iPP52	51.5	13.3	1.7	12.2	5.6	1.4	5.2	4.1	5.0
iPP76	76.3	9.8	0.0	7.0	2.0	0.0	1.8	0.6	2.5
iPP87	87.0	6.2	0.7	3.2	0.7	0.1	0.6	0.4	1.1
iPP91	90.6	6.5	0.4	1.4	0.3	0.1	0.1	0.1	0.5

entirely for such slow decrease in isospecificity.

The application of TREF visually elucidates the changes in the distribution of isospecific active sites shown in Figure 3 and 4. There exist two remarkable peaks in these TREF diagrams. The higher temperature (ca. 115 °C) peak corresponds to a higher isospecific active site, and the lower (ca. 108 °C) to lower isospecific site. The intensity of the higher peak gradually decreases with increasing extraction time. Interestingly, the lower peak grows with increasing extraction time of the internal donor. The growing suggests that the higher isospecific active site is converted to the lower one by the extraction of the internal donor. In order to study this phenomenon in detail, the iPPs were fractionated into two fractions (denoted as Fraction I and Fraction II) in two temperature ranges of 90 ~ 112 °C and 112 ~ 135 °C, respectively. Fractions I and II are produced with the lower and higher isospecific active site, respectively, permiting the estimation of the [C*] for each site type. The characterization and the kinetic data are summarized in Table 2 and 3. It appears that the [C*] of the lower isospecific site increases as the [C*] for the higher isospecific site decreases. In particular, this tendency is remarkable in the iPP series made with Cat-A, in good agreement with the changes in the TREF profiles. The TREF results demonstrate that the higher isospecific active site is converted into the lower one by the extraction of the internal donor.

In conclusion, TREF has been proved to be quite effective to evaluate the change of stereospecificity of active sites.

TREF Application to Polymer Degradation Behavior

PP is very vulnerable against oxidation. This process is called "degradation" and it is a very important practical issue. Although many researchers have been involved in developing industrial polypropylene resins,

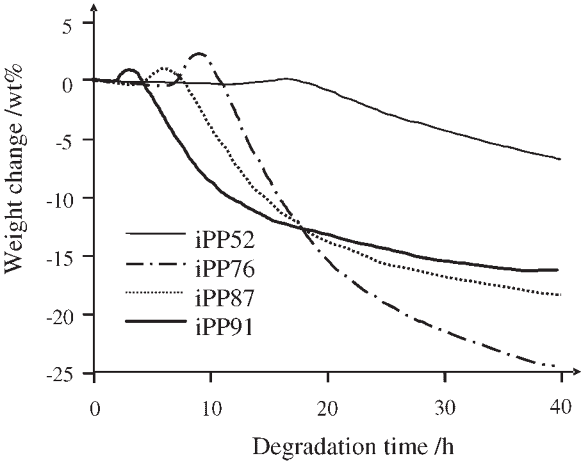

Figure 6.
Thermogravimetric analysis results of fractionated iPPs.

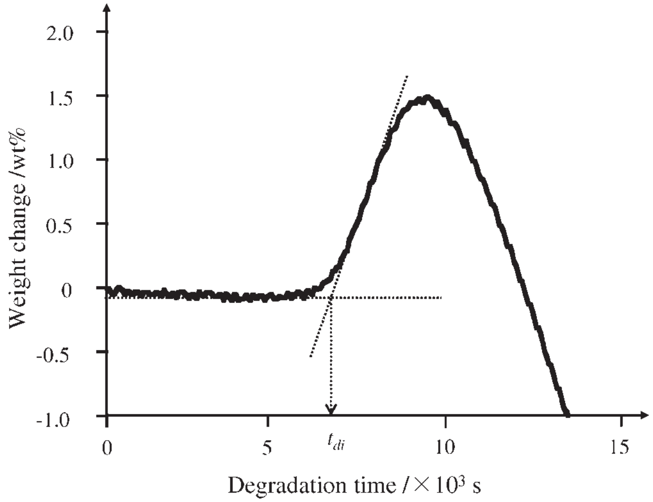

Figure 7.
An example of weight change curve showing a determination of the durations of induction period (t_{di}).

polypropylene degradation has not been comprehensively studied with the viewpoint of a stereochemical reaction. The reason for this is that it is difficult to prepare a series of polypropylene resins with various tacticities.

As shown in Figure 5, we succeeded in the synthesis of iPP with broad isotacticity distribution using the $TiCl_3/MgCl_2$ catalyst.[9] Four kinds of iPP with different isotacticities were easily obtained from the fractionation of this iPP by TREF. The fraction ratios and molecular weights are summarized in Table 4. The nomenclature of the fractionated iPP is as follows: iPP91 denotes iPP with the pentad fraction (mmmm) of ca. 91 mol%. All pentad fractions of the iPPs are shown in Table 5.

The dependence of thermal oxidative degradation on the isotacticity was carried out with these iPPs. It is noticed here that all of the thermal oxidations have been

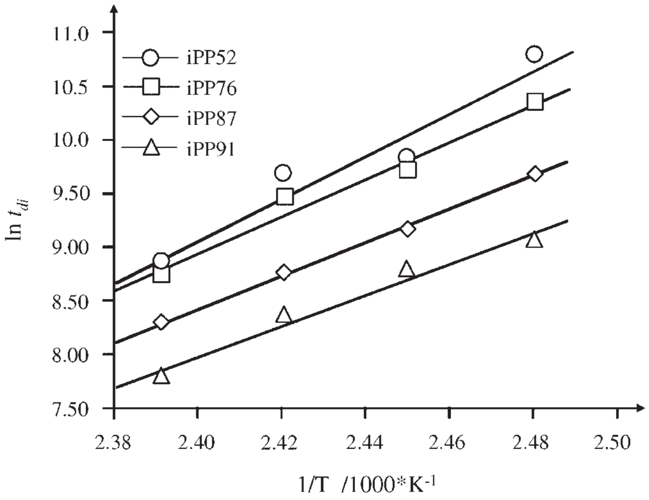

Figure 8.
Arrhenius plots of t_{di} for thermal oxidative degradation of iPPs.

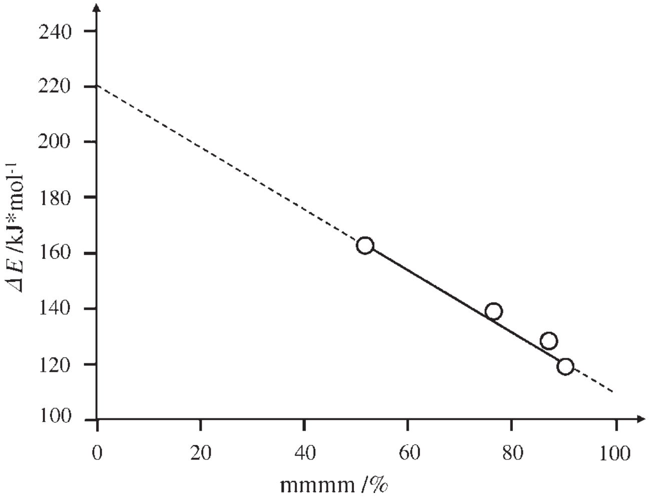

Figure 9.
Activation energy (ΔE) versus meso pentad fraction (mmmm) for all of degraded iPPs.

performed at 130 °C. At such higher temperature,[14,15] the degradation initiator (radical species) can be diffused sufficiently in the iPP crystalline part, and the degradation reaction proceeds homogeneously in the whole of the iPP sample.

These weight change curves measured by TGA are shown in Figure 6. The thermal oxidative degradation was performed at a constant temperature (130 °C) in atmospheric air. The weight changes of iPPs display multi-stages with advance of degradation.[16,17] A period of constant weight, namely induction period, is initially seen, and then the weight is increasing by oxidation. Beyond a given maximum wight, weight loss starts to take place as some components are volatilized, and finally the mass balance becomes negative. Figure 6 shows that the weight increase, or end of the induction period, starts earlier as the mmmm becomes higher. These results show that the initiation of the degradation reaction depends strongly on the isotacticity. As illustrated in Figure 7, the duration of induction period (t_{di}) was defined as the time (in seconds) at the intersection of the tangent at the inflection point with the plateau line of induction period. The t_{di} was determined using the weight change curves obtained from the measurements at four constant temperatures (130, 135, 140 and 145 °C). These values have been fitted to an Arrhenius expression to obtain the apparent activation energy (ΔE). As shown in Figure 8, the t_{di} apparently obeys the Arrhenius law within the chosen temperature limits. All the obtained ΔE are plotted against the mmmm in Figure 9.

It appears that ΔE is inversely proportional to mmmm. The relationship obeys the following equation:

$$\Delta E(\mathrm{kJ/mol}) = -1.24 \times [\mathrm{mmmm}] + 220 \qquad (3)$$

This result implies that the stability of iPP can be predicted without thermal degradation testing using the simple Equation (3). Actually the availability of this equation has been confirmed by using a higher iPP (mmmm = 95 mol%, $\overline{M}_n = 1.8 \times 10^4$ g/mol, $\overline{M}_w/\overline{M}_n = 4.9$).

Therefore, we demonstrated that TREF can be very useful for the study the influence of isotacticity on the degradation of polypropylene.

Conclusions

TREF has been regarded as a powerful technique for the structural study of semicrystalline polymers. In this paper, two examples of TREF applications were reported for isospecific propylene polymerization kinetics and for degradation behavior of isotactic polypropylene. TREF could detect the conversion from higher to lower isospecific sites by extraction of internal donor and estimate an inverse correlation between isotacticity and degradation rate of isotactic polypropylene. It was found that TREF possesses an extensive applicability to different problems in polymer science.

[1] M. Kakugo, T. Miyatake, K. Mizunuma, Y. Kawai, *Macromolecules* **1988**, *21*, 2309.

[2] M. Kakugo, T. Miyatake, T. Mizunuma, *Macromolecules* **1991**, *24*, 1469.

[3] M. Kioka, H. Makio, A. Mizuno, N. Kashiwa, *Polymer* **1994**, *35*, 580.

[4] H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol. Rapid Commun.* **2001**, *22*, 326.

[5] H. Matsuoka, B. Liu, H. Nakatani, I. Nishiyama, M. Terano, *Polym. Int.* **2002**, *51*, 781.

[6] S. Suzuki, Y. Nakamura, A. K. Hasan, B. Liu, M. Terano, H. Nakatani, *Polym. Bull.* **2005**, *54*(4–5), 311.

[7] H. Nakatani, S. Suzuki, T. Tanaka, M. Terano, *Polymer* **2005**, *46*(26), 12366.

[8] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.

[9] F. Grisi, P. Longo, A. Zambelli, J. A. Ewen, *J. Mol. Catal.* **1996**, *140*, 225.

[10] M. Matsuoka, S. Matsui, M. Mitani, J. Saito, K. Tsuru, N. Kashiwa, T. Fujita, *J. Mol. Catal.* **2001**, *169*, 99.

[11] T. Keii, M. Terano, K. Kimura, K. Ishii, *Makromol. Chem.,Rapid Commun.* **1987**, *8*, 583.

[12] H. Mori, H. Saito, M. Terano, *Macromol. Chem. Phys.* **1988**, *199*, 55.

[13] H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol. Rapid Commun.* **2001**, *22*, 326.

[14] L. Achimsky, L. Audouin, J. Verdu, J. Rychly, L. Matisova-Rychla, *Polym. Degrad. Stab.* **1997**, *58*, 283.

[15] P. Tiemblo, J. M. Gómez-Elvira, S. Garcia Beltrán, L. Matisova-Rychla, J. Rychly, *Macromolecules* **2002**, *35*, 5922.

[16] L. Audouin, L. Achimsky, J. Verdu, in: "*Handbook of Polymer Degradation*", 2d ed., S. Halim Hamid, Ed., Marcel Dekker, New York 2000, p. 727.

[17] J. Rychly, L. Matisova-Rychla, K. Csmorova, L. Achimsky, L. Audouin, A. Tcharkhtchi, J. Verdu, *Polym. Degrad. Stab.* **1997**, *58*, 269.