Crystallization and Melting Characteristics of Metallocene Isotactic Polypropylenes

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ABSTRACT: The measurement of crystallization and melting behaviors under constant rates of cooling and heating and the Avrami's analysis of isothermal crystallization were carried out for various metallocene- (MET-PP) and Ziegler-Natta-catalyzed (ZN-PP) random polypropylene copolymers with various ethylene contents. Both the melting point T_m and the crystallization temperature T_c decrease with increasing ethylene content. Compared at the same ethylene content, both are lower for MET-PP because of the higher uniformities of stereoirregular bonds and copolymerization bonds. T_m and T_c show a linear correlation, and compared at the same T_c, T_m of MET-PP is lower than that of ZN-PP. This is because MET-PP has narrower distributions of isotactic sequence length and hence of lamellar thickness than ZN-PP. The heat of fusion and the latent heat of crystallization decrease with ethylene content. At the same ethylene content, both are lower for MET-PP, owing also to the higher uniformities of stereoirregular bonds and copolymerization bonds. From the Avrami's analysis, it is assumed that there is little difference in crystallization modes of both catalyst PPs. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1851–1857, 2002

Key words: isotactic polypropylene; metallocene catalyst; Ziegler-Natta catalyst; crystallization characteristics; melting characteristics

INTRODUCTION

In the processing of a semicrystalline polymer, a molten resin is shaped by the flow and fixed by the solidification. In this process, the macroscopic shaping is accompanied by the microscopic change of the aggregation state of molecular chains, namely the higher order structure. The controlling factor of the higher order structure is also rheological and crystallization characteristics. Namely, in the processing of a semicrystalline polymer, the rheological and crystallization characteristics deeply participate in all the phases of macroscopic shaping and microscopic change of higher order structure.

On the other hand, there are many cases where the melting characteristics participate in the product properties by the use of the processed article. The melting characteristics of a semicrystalline polymer determine the heat resistance of a processed article and participate in the heat-sealing characteristics when used as a sealant.

In the previous article,[1] the rheological characteristics of isotactic polypropylenes (MET-PP) prepared by use of a metallocene catalyst were studied. The present study briefly reports the study on the crystallization and melting characteristics of MET-PPs. The measurement by DSC of crystallization and melting behaviors under constant rates of cooling and heating and the Avrami's analysis[2] of isothermal crystallization

Table I   Characteristics of Samples and DSC Results

Catalyst	Sample Name	Ethylene Content (wt %)	MFI (g/10 min)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)
				DSC Results			
Metallocene	MET-1	0	1.66	112.4	146.8	81.3	83.5
	MET-2	0	2.16	112.0	146.8	83.2	86.2
	MET-3	0	6.3	110.1	150.1	84.4	88.9
	MET-4	0	8.2	111.6	149.7	86.5	90.0
	MET-5	1.4	4.1	102.2	137.7	72.7	74.7
	MET-6	1.7	4.6	103.5	136.2	69.7	73.0
	MET-7	1.9	4.9	99.1	134.7	69.2	73.2
	MET-8	3.2	7.3	91.2	126.5	58.1	60.7
	ZN-1	0	8.5	120.5	163.1	99.9	105.4
	ZN-2	0.5	2.12	112.4	157.7	91.0	95.1
Ziegler-Natta	ZN-3	3.7	2.39	102.5	143.7	71.5	73.5
	ZN-4	3.7	7.6	107.7	146.3	77.5	79.5
	ZN-5	5.5	7.4	98.2	136.8	62.9	64.5

were carried out for various metallocene- and Ziegler-Natta-catalyzed (ZN-PP) random polypropylene copolymers with various ethylene contents and the crystallization and melting characteristics of MET-PP are made clear.

EXPERIMENTAL

Samples

Table I shows the characteristics of samples. MET-PPs were prepared by use of a methylalumoxane (MAO)-supported metallocene-PP catalyst and ZN-PPs were prepared by use of an MgCl$_2$-supported titanium catalyst. The ethylene content was obtained from the absorbance of a 720-cm^{-1} band in the infrared absorption spectrum measured by use of an infrared spectrometer IR-700 Type (JASCO, Japan). Melt flow index (MFI) was measured by use of a melt indexer X416 Type (Takara Thermistor Instruments Co. Ltd., Japan) under a 2160-g load at 230°C, according to ASTM D1238-62T.

Measurements

Crystallization and Melting Behaviors at Constant Rates of Cooling and Heating

All the samples in Table I were measured. Several pellets between two slide glasses were put on a hot plate at 210°C, melted, and pressed with a

pincette. Then they were taken off and cooled in ambient air and a 0.3-mm-thick sheet was obtained. The crystallization and melting behaviors were measured by a differential scanning calorimeter, DSC-6200R Type (Seiko Instruments, Japan). A circular specimen weighing about 10 mg was cut from the sheet specimen and put into a sample pan and melted in the furnace in a nitrogen atmosphere at 230°C for 10 min, followed by cooling at a rate of 10°C/min, and the crystallization thermogram was measured. The peak temperature and area of the exothermic curve were taken as the crystallization temperature T_c and the latent heat of crystallization ΔH_c, respectively. For the calculation of ΔH_c, 70°C was chosen as the low temperature limit of the baseline. As soon as the temperature reached 30°C, it was heated at a rate of 10°C/min and the melting thermogram was measured. The peak temperature and area of the endothermic curve were taken as the melting point T_m and the heat of fusion ΔH_m, respectively. For the calculation of ΔH_m, 60°C was chosen as the low temperature limit of the baseline. These measurement results are shown in Table I.

Isothermal Crystallization (Avrami's Analysis)

As samples for the Avrami's analysis, six samples of three pairs of MET-PPs and ZN-PPs which have equivalent T_c's [MET-1 (T_c = 112.4°C)/ZN-2 (112.4°C), MET-5 (102.2°C)/ZN-3 (102.5°C),

MET-7 (99.1°C)/ZN-5 (98.2°C)] were chosen. Sheets of 0.3 mm thick were molded from these samples by the same manner as above. They were melted in the furnace of the DSC apparatus in a nitrogen atmosphere at 230°C for 10 min, followed by cooling at a rate of 100°C/min to crystallization temperatures T_c's (three to four temperatures of 5°C intervals starting from a temperature near T_c) and the isothermal crystallization thermogram (the time change of exothermic curve) was measured.

According to Avrami,[2] the change of crystalline fraction x with time t in isothermal crystallization is expressed by the following equations:

$$1 - x = \exp(-kt^n) \qquad (1)$$

$$\ln(1 - x) = -kt^n \qquad (2)$$
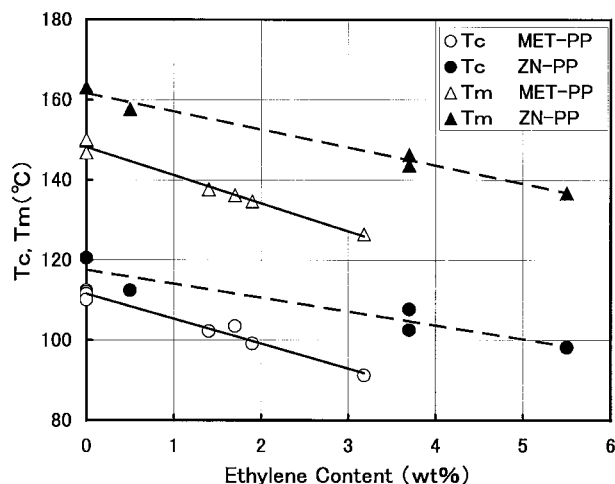
$$\log\{-\ln(1 - x)\} = \log k + n\log t \qquad (3)$$

where k and n are constants.

Equation (3) shows that the plot of $\log\{-\ln(1 - x)\}$ against $\log t$ gives a straight line and the Avrami's exponent n can be obtained from the slope. The crystallization half-time $t_{1/2}$ was obtained from the time where $x = 0.5$. The Avrami's exponent n is determined by the crystal growth mode and the relation between n and the growth mode is shown in Table II.

RESULTS AND DISCUSSION

Crystallization and Melting Behaviors at Constant Rates of Cooling and Heating

Figure 1 shows the dependence of crystallization temperature T_c and melting point T_m on ethylene content. Both T_c and T_m decrease with increasing ethylene content, and compared at the same eth-

Table II Nucleation Mechanism and *n* Value

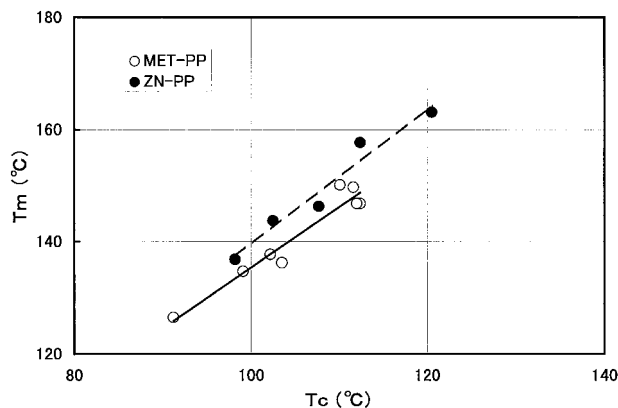| Growth Mode	Homogeneous Nucleation	Heterogeneous Nucleation
3-Dimensional (Spherical)	4	3
2-Dimensional (Disklike)	3	2
1-Dimensional (Needlelike)	2	1

Figure 1 Dependence of crystallization temperature T_c and melting point T_m on ethylene content.

ylene content, MET-PP shows 10–20°C lower values than ZN-PP. This is assumed to be due to the high content of regioirregular bonds of MET-PP. Mori and Saito[3] also obtained similar results for T_m's of ethylene-propylene random copolymers of MET-PP and ZN-PP. Bond and Spruiell[4] found that T_m, T_c, and equilibrium melting point T_m^0 of homo-PP of MET-PP are lower than those of controlled rheology-type ZN-PP. They assume the following reason: Because MET-PP is polymerized by a single-site catalyst, its intermolecular distribution of defects (stereoirregular and regioirregular bonds: hereinafter called stereoirregular bonds altogether) is uniform. Accordingly, at the time of crystallization, the defects are rejected from or incorporated in lamellar crystals, which results in thinning of the lamellae or in disordering of crystalline quality. In fact, Huang and Alamo[5] report that compared at the same crystallization temperature, the lamellae of MET-PP are thinner than those of ZN-PP. The differences of T_c and T_m between both PPs in Figure 1 tend to increase with increasing ethylene content. In random PP copolymers with ethylene, the intermolecular distribution of copolymerization bonds of MET-PP is more uniform than that of ZN-PP and hence the same matter as for the stereoirregular bonds mentioned above can be said. Namely, the differences in T_c and T_m between both PPs are influenced only by the difference in the intermolecular distribution of the stereoirregular bonds in the case of homo-PPs. On the other hand, the difference in the intermolecular distribution of the copolymerization bonds is

Figure 2 Relation between melting point T_m and crystallization temperature T_c.

put on it in the case of copolymers. Accordingly, the differences of T_c and T_m between both PPs increase with increasing ethylene content.

Figure 2 shows the relation between the melting point T_m and the crystallization temperature T_c. T_m is almost in a linear relationship with T_c for each PP, and compared at the same T_c, T_m of MET-PP tends to be lower than that of ZN-PP. According to Hoffman et al.,[6,7] T_m of lamellar crystal is expressed by the following equation:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_f l} \right) \qquad (4)$$

where T_m^0 is the equilibrium melting point, σ_e is the surface free energy of fold plane of lamella, Δh_f is the heat of fusion, and l is the thickness of lamella. Because the actual measured melting point is the temperature where crystals completely vanish, the melting point is not related with crystals with mean lamellar thickness l but with crystals with a step height of βl. The value of β is determined by the distribution of l. When the distribution of l is sharp, it is near unity and it is usually 1–1.5. Namely, the melting point T_m observed usually is expressed by the following equation:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_f \beta l} \right) \qquad (5)$$

Because the distributions of stereoirregular bonds and copolymerization bonds of MET-PP are more uniform than those of ZN-PP, the distribution of crystallinity (isotactic sequence length) of the former is narrower than that of the latter.[8]

Accordingly, the thickness of lamellae of the former is not only thinner but also more uniform than that of the latter, and hence, β in eq. (5) is lower for the former, which is assumed to lead a lower observed melting point T_m for the former.

Figure 3 shows the dependence of the latent heat of crystallization ΔH_c and the heat of fusion ΔH_m on ethylene content. ΔH_c and ΔH_m show nearly similar values (ΔH_m is slightly higher) and decrease with increasing ethylene content. Compared at the same ethylene content, MET-PP shows lower values of ΔH_c and ΔH_m than ZN-PP. Two reasons are considered for lower values of ΔH_c and ΔH_m of MET-PP: One reason is because of lower crystallinity and the other reason is because of the disordering of crystalline quality. To examine this cause, sheets were extruded from MET-2 and ZN-2 samples under the same conditions and their crystallinities were measured. The crystallinities of MET-2 and ZN-2 samples were 58.4 and 57.7%, respectively, which are nearly the same. Accordingly, the reason for lower values of ΔH_c and ΔH_m of MET-PP is assumed to be because of the latter cause: the disordering of crystalline quality. As mentioned above, this reason is assumed to be as follows: Because the distributions of stereoirregular bonds and copolymerization bonds of MET-PP are more uniform than those of ZN-PP, the parts of stereoirregular bonds and copolymerization bonds are not rejected from but incorporated in the lamellar crystals at crystallization.
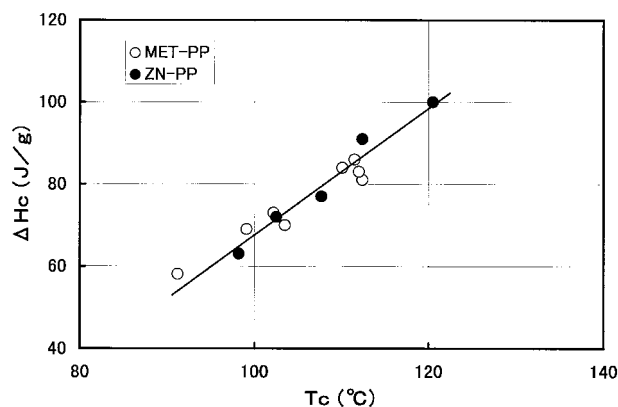
Figure 4 shows the relation between the latent heat of crystallization ΔH_c and the crystallization temperature T_c. Irrespective of the kind of cata-
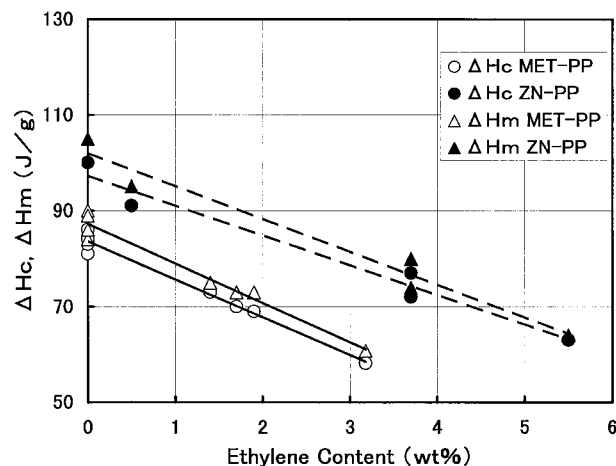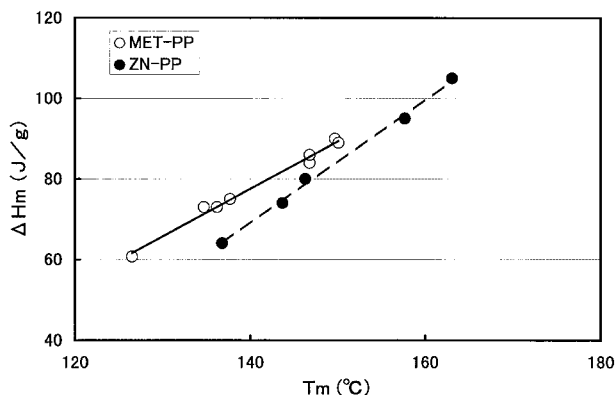

Figure 3 Dependence of latent heat of crystallization ΔH_c and heat of fusion ΔH_m on ethylene content.

lyst, they show a linear relationship, and when T_c is higher, ΔH_c is also higher.

Figure 5 shows the relation between the heat of fusion ΔH_m and the melting point T_m. Both show a different linear relationship for each catalyst and when T_m is higher, ΔH_m is also higher. Compared at the same T_m, ΔH_m of MET-PP is higher than that of ZN-PP and the difference is larger as the ethylene content is higher and T_m becomes lower. As the reason why, compared at the same T_m, MET-PP shows higher ΔH_m than ZN-PP, particularly in the low T_m range, the low precision of evaluation method of ΔH_m is considered. As mentioned in the experimental section, 60°C was chosen for convenience as the low limit temperature of baseline of thermogram for the determination of ΔH_m. MET-PP has a narrow distribution of crystallinity,[8] contains few low melting point components, and melts in a relatively narrow temperature range. On the other hand, ZN-PP, particularly one with a high ethylene content and hence with a low melting point, has a wide crystallinity distribution, contains many low melting point components, and is assumed to have a possibility to contain a considerable amount of low melting point crystals which melt below 60°C. Accordingly, it is assumed that the crystals with a melting point below 60°C were neglected and ΔH_m was apparently evaluated lower. In this sense, it should be explained that compared at the same T_m, ΔH_m of MET-PP is not higher than that of ZN-PP but ΔH_m of ZN-PP was evaluated lower than the true value. It may be considered that ΔH_m of MET-PP is estimated more exactly than that of ZN-PP. The influence of this kind of catalyst scarcely appears for the latent heat of crystallization ΔH_c in Figure 4. This is assumed to be

**Figure 5** Relation between heat of fusion ΔH_m and melting point T_m.

because the error in estimation of ΔH_c caused by the drawing manner of baseline is small because the crystallization occurs in a very narrower temperature range than the melting. Furthermore, Figure 3 shows that compared at the same ethylene content, ΔH_c and ΔH_m of MET-PP are lower than those of ZN-PP. These differences shall further increase if the error in estimation of ΔH_m caused by the drawing manner of baseline is considered and the conclusion from Figure 3 that the crystalline quality of MET-PP is more disordered than that of ZN-PP is not necessary to be changed.

Avrami's Analysis

Figure 6(a,b) shows Avrami's plots of MET-1 and ZN-2 samples, respectively. Although the latter shows linear relationships in all regions of crystallization temperature, the former shows breakings of lines and the slopes of lines at high temperatures become easier. Only the MET-1 sample shows these breakings and other samples show linear relationships in almost all ranges of crystallization temperature.

Figure 7 shows the relation between the crystallization half-time $t_{1/2}$ and crystallization temperature T'_c. Although $t_{1/2}$'s of MET-PP and ZN-PP, which have an equivalent crystallization temperature T_c measured under a constant cooling rate, are equivalent at T'_c near T_c, MET-PP becomes to show longer $t_{1/2}$ than ZN-PP with increasing T'_c. This is because of the lower T_m of MET-PP compared at the same T_c; the degree of supercooling, ΔT (= $T_m - T'_c$), of MET-PP is lower than that of ZN-PP compared at the same T'_c. Bond and Spruiell[4] obtained a result for

Figure 4 Relation between latent heat of crystallization ΔH_c and crystallization temperature T_c.
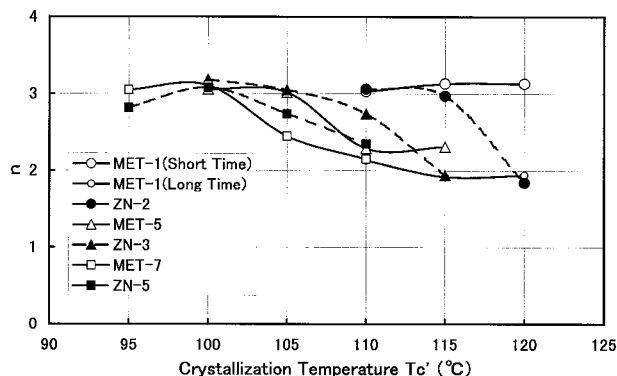
(a)

(b)
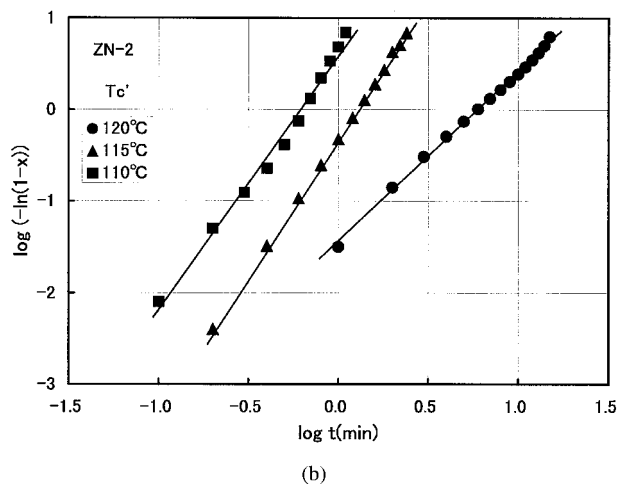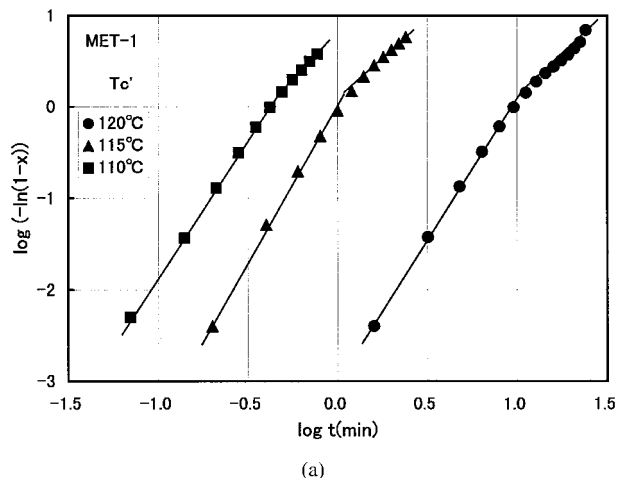
Figure 6 (a) Avrami plots for MET-1; (b) Avrami plots for ZN-2.

homo-PPs with different T_c that $t_{1/2}$ of an MET-PP is longer than that of a controlled rheology-type ZN-PP.
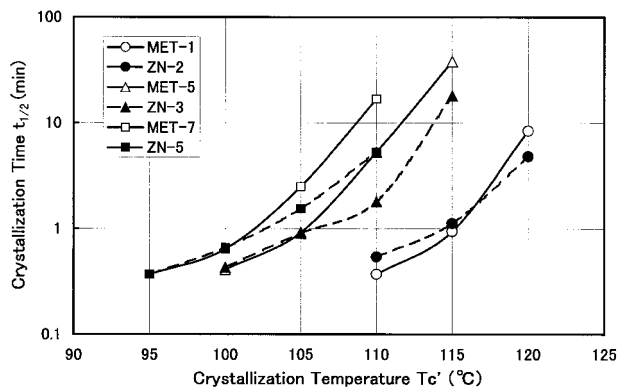
Figure 7 Dependence of crystallization time $t_{1/2}$ on crystallization temperature T'_c.

Figure 8 Dependence of Avrami's exponent n on crystallization temperature T'_c.

Figure 8 shows the relation between the Avrami's exponent n and the crystallization temperature T'_c. The value of n is about 3 at low T''_c's, increases with increasing T'_c, and becomes about 2 at high T''_c's. These tendencies of MET-PP and ZN-PP with nearly equivalent T_c scarcely differ from each other and both PPs show similar behaviors. The crystallization temperature T'_c at which n begins to decrease is lower as T_c is lower. As shown in Table II, when $N = 3$, the crystal growth mode is three-dimensional (spherulite) in the case of heterogeneous nucleation and two-dimensional (disklike crystal) in the case of homogeneous nucleation. When $N = 2$, the growth mode is two-dimensional (disklike crystal) in the case of heterogeneous nucleation and one-dimensional (needlelike crystal) in the case of homogeneous nucleation. The nucleation of usual PP is considered to be heterogeneous because it contains impurities such as catalyst residues and additives. Accordingly, it is assumed from the experimental results mentioned above that spherulites are formed at low temperatures near T_c and disklike crystals are formed at high temperatures 10–15°C higher than T_c. These disklike crystals may be considered to be two-dimensional spherulites. At intermediate temperatures, intermediate form crystals or a mixture of spherulites and two-dimensional spherulites are assumed to be formed. The reason spherulites are formed at low temperatures and disklike crystals are formed at high temperatures is assumed to be because the sample thickness of DSC measurements is thin (0.3 mm). It is assumed that in the case of crystallization at low temperatures, the crystals formed are small and grow to spherulites. On the other hand, in the case of crystallization at high temperatures, the crystals formed are large

and cannot grow to spherulites because of the limitation of thickness and become disklike crystals. Anyway, it may be said that the temperature change of crystallization mechanism scarcely differs between MET-PPs and ZN-PPs.

CONCLUSION

Out of rheological and crystallization characteristics which are governing factors of structure formation in the processing of semicrystalline polymers, the latter was studied in the present study. The measurement of crystallization and melting behaviors under constant rates of cooling and heating and the Avrami's analysis of isothermal crystallization were carried out for various metallocene- (MET-PP) and Ziegler-Natta-catalyzed (ZN-PP) random polypropylene copolymers with various ethylene contents.

1. Both the melting point T_m and the crystallization temperature T_c decrease with an increase in the ethylene content. The degree of the decrease is higher for T_m than for T_c. Compared at the same ethylene content, both are lower for MET-PP. The differences of T_m and T_c between the catalysts increase with increasing ethylene content. This is assumed to be due to the uniform intermolecular distribution of defects such as stereoirregular bonds and copolymerization bonds for MET-PP. Hence, at the time of crystallization, the defects are rejected from or incorporated in lamellar crystals, which results in thinning of the lamellae or in disordering of crystalline quality. Accordingly, the low temperature heat-sealing characteristic of a film prepared from MET-PP is superior to that from ZN-PP.

2. The melting point T_m and the crystallization temperature T_c are in a linear relationship for each PP. Compared at the same T_c, T_m of MET-PP is lower than that of ZN-PP. This is because MET-PP has a narrower distribution of isotactic sequence length and hence has thinner lamellar thickness and more uniform distribution.

3. Both the heat of fusion ΔH_m and the latent heat of crystallization ΔH_c decrease with increasing ethylene content. For the same sample, the former is slightly higher. Compared at the same ethylene content, both heats are lower for MET-PP. This is assumed to be also due to the difference in the intermolecular distributions of the defects such as stereoirregular bonds and copolymerization bonds and due to the more disordered crystalline quality of MET-PP.

4. Irrespective of catalysts, the Avrami's exponent n is about 3 at low-crystallization temperatures, decreases with increasing crystallization temperature, and becomes about 2 at high temperatures. From this, the growth mode is three-dimensional (spherulite) at low crystallization temperatures and two-dimensional (two-dimensional spherulite) at high crystallization temperatures.

REFERENCES

1. Fujiyama, M.; Inata, H. J Appl Polym Sci 2002, 84, 2157.
2. Avrami, M. J Chem Phys 1939, 7, 1103; J Chem Phys 1940, 8, 212.
3. Mori. K.; Saito, J. Seikei-Kakou 1996, 8, 649.
4. Bond, E. B.; Spruiell, J. E. SPE Tech. Pap., 55th ANTEC, 1997, 43, 1750.
5. Huang, W.; Alamo, R. G. SPE Tech. Pap., 58th ANTEC, 2000, 46, 3546.
6. Hoffman, J. D.; Lauritzen, J. I. J Res Nat Bur Stands 1961, 65A, 297.
7. Hoffman, J. D.; Weeks, J. J. J Res Nat Bur Stands 1962, 66A, 13.
8. Ushioda, T.; Fujita, H.; Saito, J. Kagaku Kogyo 1998, 36, 123.