

REFERENCES

- Ahn, S.H., Cho, C.B., and Lee, K.Y. (2000). The kinetics shear-induced crystallization on poly (ethylene terephthalate). <u>SPE Tech Papers</u>, 341-350.
- Chan, T.W. and Isayev, A.I. (1994) Quiescent polymer crystallization: modeling and measurements. Polymer Engineering and Science, 34(6), 461-471.
- Chuah, H.H. (2001). Modern Polyesters. London: John Wiley, 75-80.
- Chuah, H.H. (2001). Crystallization kinetics of poly(trimethylene terephthalate). <u>Polymer Engineering and Science</u>, 41, 308-315.
- Chung, W.T., Yeh, W.J., and Hong, P.D. (2002). Melting behavior of poly (trimethylene terephthalate). <u>Journal of Applied Polymer Science</u>, 83, 2426-2433.
- Churdpunt, Y. and Isayev, A.I. (1999). Shear-induced crystallization in injection moldings of Ziegler-Natta and metallocene based isotactic polypropylenes. <u>SPE Tech Papers</u>.
- Guo, J. and Narh, K.A. (2002). Simplified model of stress-induced crystallization kinetics of polymers. <u>Advances in Polymer Technology</u>, 21(3), 214-222.
- Huang, J.M. and Chang, F.C. (2000). Crystallization Kinetics of Poly(trimethylene terephthalate). Journal of Polymer Science PartB: Polymer Physics, 38, 934-941.
- Jerschow, P. and Janeschitz-Kriegl, H. (1997). The role of long molecules and nucleating agents in shear-induced crystallization of isotactic polypropylenes. International Polymer Processing, 12, 72-77.
- Kakani, M. (1997). <u>An experimental study of flow-induced crystallization in high</u> <u>density polyethylene and polypropylene</u>. M.S. Thesis in Polymer Science, Faculty of the Graduate College, Oklahoma State University.
- Kim, S.P. and Kim, S.C. (1993). Crystallization kinetics of poly (ethylene terephthalate): memory effect of shear history. <u>Polymer Engineering and</u> <u>Science</u>, 33(2), 83-91.
- Marand H. and Xu J. (1998). Determination of the Equilibrium Melting Temperature of Polymer Crystals: Linear and Nonlinear Hoffman-Weeks Extrapolations. <u>Macromolecules</u>, 31, 8219-8229.

- Masubuchi,Y. (2001). Thermal analysis of shear induced crystallization by shear flow thermal rheometer: isothermal crystallization of polypropylene. <u>Polymer</u>, 42, 5023-5027.
- Moitzi, J. and Skalicky, P. (1993). Shear-induced crystallization of isotactic polypropylene melts: isothermal WAXS experiment with synchroton radiation. <u>Polymer</u>, 34(15), 3168-3172.
- Myung, H.S., Yoon, W.J., Yoo, E.S., Kim, B.C., and Im, S.S. (2001). Effect of shearing on crystallization behavior of poly(ethylene terephthalate). Journal of Applied Polymer Science, 80, 2640-2646.
- Ness, J.N. and Liang, J.Z. (1993). A study of rheological properties and crystallization behavior for HDPE melts during extrusion. <u>Journal of</u> <u>Applied Polymer Science</u>, 48, 557-561.
- Patel, R.M. and Spruiell J.E. (1991). Crystallization kinetics during polymer processing-analysis of available approaches for process modeling. Polymer Engineering and Science, 31, 730-737.
- Sherwood (1977). <u>The effect of shear polymer crystallization kinetics</u>. Ph.D. Dissertation in Polymer, Chemistry, University of Massachusetts.
- Supaphol, P. and Spruiell, J.E. (2000). Regime crystallization in syndiotactic polypropylene: re-evaluation of the literature data. <u>Poymer</u>, 41, 1205-1216.
- Supaphol, P. (2001). Application of the Avrami, Tobin, Malkin, and Urbanovici-Segal macrokinetic models to isothermal crystallization of syndiotactic polypropylene. <u>Thermochimica Acta</u>, 370, 37-48.
- Supaphol, P. and Lin, J.S. (2001). Crystalline memory effect in isothermal crystallization of syndiotactic polypropylenes: effect of fusion temperature on crystallization and melting behavior. <u>Polymer</u>, 42, 9617-9626.
- Supaphol, P. (2001) Crystallization and melting behavior in syndiotactic polypropylene: origin of multiple melting phenomenon. <u>Journal of Applied</u> <u>Polymer Science</u>, 82, 1083-1097.
- Sura, R.S., Desai, P., and A.S. Abhiraman. (2001) Oriented crystallization in fiber formation: Inferences form the structure and properties of melt spun syndiotactic polypropylene filaments. <u>Journal of Applied Polymer Science</u>, 81, 2305-2317.

- Watanabe, K., Nagatake, W., Takahashi, T., Masubuchi, Y., Takimoto, J., and Koyama, K. (2003). Direct observation of polymer crystallization process under shear by shear flow observation system. <u>Polymer Testing</u>, 22, 101-108.
- Wolkowicz, M.D. (1983). <u>Crystallization and morphological phenomenon of sheared poly (1-butene) melts</u>. Ph.D. Dissertation in Polymer Science and Engineering, the Graduate school, University of Massachusetts.
- Wu P.L. and Woo E.M. (2002). Linear versus non-linear determine equilibrium melting temperature of poly(trimethylene terephthalate) and Miscible blend with Polyether imide. <u>Journal of Polymer Science PartB: Polymer Physics</u>, 40, 571-581.
- Wu P.L. and Woo E.M. (2003). Correlation between Melting Behavior and Ringed Spherulites in poly(trimrthylene terephthalate). Journal of Polymer Science PartB: Polymer Physics, 41, 80-93.
- Wu, J., Schultz, J.M., Samon, J.M., Pangelinan, A.B., Chuah, H.H. (2001). In situ study of structure development in poly(trimethylene terephthalate) fibers during stretching by simultaneous synchrotron small-and wide-angel X-ray scattering. <u>Polymer</u>, 42, 7141-7151.

APPENDIX A

Origin of multiple peak of PTT



Figure A1 Plots of the scaled observed melting temerature $[M = T_m^{\circ}/(T_m^{\circ} - T_m)]$ versus the scaled crystallization temperature $[X = T_m^{\circ}/(T_m^{\circ} - T_c)]$ for various choices of the seeded equilibrium melting temperature (T_m°) of PTT $(T_m - T_c)$ data 188 to 215°C).



Figure A2 The variation of the thickening coefficient (β^m) as a function of the seeded equilibrium melting temperature ($T_m - T_c$ data 188 to 215°C).

APPENDIX B

Calculation in capillary rheometer

The load on the plunger and the plunger speed were converted into apparent shear stress and shear rate at the wall respectively by using the following equations involving the geometry of the capillary and the barrel:

$$\tau_{\rm w} = \frac{FD_{\rm C}}{4A_{\rm p}L_{\rm c}} \tag{b1}$$

where τ_w is apparent shear stress at the wall; *F* is the force acting on the plunger; A_p is cross sectional area of the plunger; D_c is diameter of the capillary die; L_c is length of the capillary die:

$$\dot{\gamma}_{w} = \frac{2V_{\rho}D_{\rho}^{2}}{15D_{c}^{3}}$$
(b2)

where $\dot{\gamma}_{w}$ is apparent rate at wall; V_{p} is plunger speed; D_{b} is barrel diameter

$$\eta_a = \frac{\tau_w}{\gamma_w} \tag{b3}$$

where η_a is apparrent viscosity

The true shear rate was determined by using the Rabinowitch correction,

$$\gamma = \frac{3n+1}{4n} \cdot \gamma_{w} \tag{b4}$$

where $\dot{\gamma}_{\text{tr}}$ is true shear rate; n is Power law index. The value of *n* is the slope of the plot of log τ_{w} versus log $\dot{\gamma}_{\text{w}}$.

In this study, the Bagley correction was not necessary because the L/D ratio was 40.15, which was significantly long to neglect end effect.

APPENDIX C

Melting behavior of PTT

Table C1 Melting Behavior of PTT S0 after isothermal crystallization at 200°C recorded at a heating rate of 20°C min⁻¹. Blank is as prepared film recorded at a same heating rate

T _f	Tonset,1	$T_{\text{peak},I}$	$\Delta H_{\rm f,1}$	$T_{\rm peak,2}$	$\Delta H_{\rm f,2}$
°C	°C	°C	J.g ⁻¹	°C	$J \cdot g^{-1}$
Blank	218.3	-	-	226.3	56.0
265	216.0	219.1	26.2	228.3	27.3
270	216.2	218.6	22.2	227.7	28.0
275	216.1	219.0	24.3	228.4	27.7
280	216.1	218.4	15.8	227.7	28.7
285	215.9	218.4	23.2	228.1	29.9
290	215.9	218.2	17.4	227.7	31.2
300	215.4	217.7	16.7	227.4	35.0

Table C2 Melting Behabvior of PTT S92.1 after isothermal crystallization at 200°C recorded at a heating rate of 20°C·min⁻¹

T _f °C	T _{onset,1} °C	T _{peak,1} °C	$\Delta H_{\rm f,1}$ J·g ⁻¹	$T_{\text{peak},2}^{*}$ °C	$\Delta H_{\rm f,2}$ J·g ⁻¹
265	216.0	220.0	25.8	229.3	30.2
270	215.9	219.4	20.6	229.0	29.3
275	215.7	219.7	28.0	229.0	29.7
280	215.5	216.0	15.9	227.7	31.2
285	215.3	219.8	27.2	228.7	31.6
290	215.0	215.6	17.2	228.0	33.0
300	214.8	218.5	25.8	228.7	35.1

T _f	T _{onset,1}	$T_{peak,1}$	$\Delta H_{\mathrm{f},1}$	$T_{\rm peak,2}$	$\Delta H_{\rm f,2}$
°C	°C	°C	J·g ⁻¹	°C	J.g ⁻¹
265	216.9	220.0	22.1	230.0	30.8
270	216.0	219.8	22.3	230.0	31.4
275	215.7	219.1	22.5	229.0	30.2
280	216.0	219.4	23.7	229.3	30.2
285	215.3	218.9	23.6	228.7	30.3
290	215.2	218.6	23.5	228.7	31.1
300	214.4	218.3	21.0	228.7	32.5

Table C3 Melting Behavior of PTT S245.6 after isothermal crystallization at 200°Crecorded at a heating rate of 20°C·min⁻¹

APPENDIX D

Crystallization behavior of PTT crystallized from glassy state

Table D1 Crystallization and melting behavior of PTT shear untreated and sheartreated samples at shearing temperature = 250°C (first heating scan)

Shear rate	T_{g}	T _{cc,onset}	T _{cc}	$\Delta H_{\rm c}(-)$	T _{m,onset}	T _m	$\Delta H_{\rm f}(+)$
s ⁻¹	°C			J.g ⁻¹			
0	44.0	71.5	74.3	27.9	218.1	227.3	59.9
5t1	43.7	67.0	73.0	26.1	217.0	227.7	61.4
5t3	42.9/50.3	68.4	73.0	24.9	217.0	227.7	63.3
5t5	45.8/50.6	69.4	73.3	25.8	218.5	229.0	59.9
10t1	42.8/48.7	67.4	72.0	24.8	218.5	228.3	61.6
10t3	42.9/51.6	65.8	70.7	24.4	219.3	229.0	61.7
10t5	42.4	65.9	70.0	24.9	216.9	228.0	62.8
53.2	43.1	67.4	70.7	27.8	218.3	228.0	60.8
62.7	49.0	67.5	70.7	28.5	216.3	227.3	62.6
66.5	47.8	68.0	71.0	27.7	217.8	228.3	57.3
84.9	50.9	68.6	72.0	28.2	216.9	227.0	57.9
92.1	46.5	65.3	68.3	28.1	216.6	228.0	60.7
94.0	48.9	67.2	70.3	28.3	216.0	226.7	62.1
99.8	47.3	67.6	70.7	27.6	218.3	228.0	59.9
133.0	41.7	66.3	69.3	28.0	218.2	228.0	60.7
245.6	44.7/53.6	65.3	68.3	28.9	217.8	227.7	64.0
250.6	46.2	66.3	69.3	28.1	217.5	227.3	62.7
429.9	45.9	65.9	69.0	28.6	217.8	226.7	64.0
438.6	42.3	66.7	69.7	26.6	217.1	226.7	62.7

Shear rate	T_{g}	T _{cc,onset}	$T_{\rm cc}$	$\Delta H_{\rm c}(-)$	T _{m,onset}	T _m	$\Delta H_{\rm f}(+)$
s ⁻¹	°Č	°C	°C	J·g ⁻¹	°C	°C	J·g ⁻¹
5t1	43.5	71.0	74.3	29.4	217.8	227.0	60.9
5t3	45.2	71.4	74.3	28.9	217.2	227.7	61.2
5t5	42.6	71.0	74.3	28.7	216.7	227.3	61.2
10t1	46.0	71.8	75.0	28.1	216.7	227.7	60.4
10t3	45.3	71.3	74.3	29.2	216.9	227.3	62.1
10t5	46.3	71.7	75.0	28.4	217.0	227.7	61.6
53.2	45.5	71.0	74.0	28.7	217.6	227.3	60.8
66.5	45.1	69.5	73.3	28.4	217.5	227.3	58.2
84.9	44.7	71.2	74.3	28.8	216.0	227.3	60.3
92.1	45.4	71.7	74.7	27.5	216.5	227.7	58.9
99.8	47.1	71.5	74.3	27.9	217.5	227.7	58.5
133.0	45.8	71.6	74.7	28.4	217.5	228.0	59.1
245.6	52.2	71.4	74.3	25.2	219.0	228.3	60.7
250,6	44.9	70.8	73.7	28.6	217.4	227.0	62.2
429.9	45.6	71.1	74.3	28.4	216.5	227.0	60.4
438,6	43.7	70.0	73.0	28.5	216.8	226.7	62.6

Table D2 Crystallization and melting behavior of PTT shear untreated and sheartreated samples at shearing temperature = 250° C (second heating scan)

Table D3 Crystallization and melting behavior of PTT shear untreated and sheartreated samples at shearing temperature = 260° C (first heating scan)

Shear rate	T _g	T _{cc,onset}	T _{cc}	$\Delta H_{\rm c}(-)$	T _{m,onset}	$T_{\rm m}$	$\Delta H_{\rm f}(+)$
s ⁻¹	°C	°C	°C	J.g ⁻¹	°C	°C	J·g ⁻¹
0	45.6	71.2	74.3	29.1	216.1	226.7	62.5
70.6	48.2	67.2	70.0	29.2	217.9	228.3	62.7
105.9	43.8	66.8	69.7	29.8	218.0	228.3	63.0
141.2	50.8	68.5	71.3	28.6	216.7	227.7	62.7
211.9	50.4	68.4	71.3	28.6	217.2	228.0	64.3
268.0	49.6	67.8	70.7	28.9	216,0	227.0	63.2
469.0	51.0	68.6	71.7	29.2	216.2	227.3	64.9

Heating Rate	T _{c onset}	$T_{\rm c \ peak}$	$\Delta H_{\rm c}$	$T_{\rm m \ onset}$	$T_{m peak}$	$\Delta H_{\rm f}$
°C·min ⁻¹	°C	°C	J·g ⁻¹	°C	°C	J·g ⁻¹
10	65.7	68.5	27.1	218.3	227.2	61.2
20	71.5	74.3	28.0	218.0	227.3	61.6
30	72.1	75.5	30.7	216.2	226.5	64.0
40	73.5	77.0	32.8	215.4	225.7	64.3

Table D4 PTT samples at shear rate 0 s^{-1} melted at $T_f 260^{\circ}$ C for 5 min following by quenching in liquid nitrogen and heated at different heating rate

Table D5 PTT samples at shear rate 92.1 s⁻¹ melted at $T_f 260^{\circ}$ C for 5 min following by quenching in liquid nitrogen and heated at different heating rate

Heating Rate	T _{c onset}	$T_{\rm c peak}$	$\Delta H_{\rm c}$	T _{m onset}	$T_{\rm mpeak}$	$\Delta H_{\rm f}$
°C·min ⁻¹	°C	°C	J·g ⁻¹	°C	°C	J.g ⁻¹
10	60.6	63.5	26.8	218.9	228.0	62.9
20	65.3	68.7	28.6	216.6	228.0	61.7
30	66.3	70.0	29.6	216.3	227.5	63.5
40	68.8	72.3	30.1	216.0	227.7	62.0

Table D6 PTT samples at shear rate 245.6 s⁻¹ melted at T_f 260°C for 5 min following by quenching in liquid nitrogen and heated at different heating rate

Heating Rate	T _{c onset}	$T_{\rm c peak}$	ΔH_{c}	T _{m onset}	$T_{\rm mpeak}$	$\Delta H_{ m f}$
°C·min ⁻¹	°C	°C	J·g ⁻¹	°C	°C	J·g ⁻¹
10	61.0	63.8	30.4	217.9	227.3	69.3
20	65.2	68.3	28.9	215.0	227.7	64.0
30	63.3	70.8	25.0	216.9	227.0	62.1
40	69.7	73.0	30.6	215.8	228.3	60.7

APPENDIX E

Crystallization behavior of PTT crystallized from melt state

Table E1 PTT samples at shear rate 0 s⁻¹ melted at $T_f 260^{\circ}$ C for 5 min

Cooling Rate	Tonset	T_{peak}	$\Delta H_{\rm c}$
°C·min ⁻¹	°C	°C	$J \cdot g^{-1}$
10	194.7	184.5	51.6
20	189.5	176.6	50.4
30	182.1	167.4	49.9
40	181.9	167.9	48.9

Table E2 PTT samples at shear rate 92.1 s⁻¹ melted at $T_f 260^{\circ}$ C for 5 min

Cooling Rate	Tonset	Tpeak	ΔH_{c}
°C·min ⁻¹	°C	°C	$J \cdot g^{-1}$
10	201.3	193.0	56.2
20	196.7	184.9	54.4
30	192.9	180.5	54.3
40	189.9	177.9	53.4

Table E3 PTT samples at shear rate 245.6 s⁻¹ melted at $T_f 260^{\circ}$ C for 5 min

Cooling Rate	Tonset	$T_{\rm peak}$	ΔH_{c}
°C·min ⁻¹	°C	°C	J.g ⁻¹
10	200.2	194.1	58.7
20	197.8	189.9	55.2
30	194.5	184.5	52.8
40	192.0	180.6	53.3

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