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Crystallization Characteristics of Metallocene Low Density Polyethylene

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:
Ziegler - Natta
branching
branching 가
induction time
가
induction time 가
branching

ABSTRACT : The crystallization characteristics of metallocene linear low density polyethylene was investigated by small angle light scattering and comparison was made with Ziegler - Natta linear low density polyethylene. The special efforts were made to find out the effects of branching number, length of branching and co - monomer content of m - LLDPE on the crystallization behavior of m - LLDPE. It was found that m - LLDPE has longer induction time to start crystallization from the amorphous state than that of conventional LLDPE with similar branching number, but the rate of crystallization seems not change much in both LLDPEs. Lowering of branching number in m - LLDPE resulted in both increasing of rate of crystallization and reducing induction time to crystallize. In general, the maximum size of spherulites of m - LLDPE is bigger than that of conventional LLDPE.

Keywords : metallocene low density polyethylene, crystallization, branching number, small angle light scattering, induction time.

Ziegler - Natta 가
Ziegler - Natta 1 ,
2
3-7
Ziegler - Natta

가 가
가
Ziegler - Natta
가
가
가
가⁸⁻¹⁰
(m - LLDPE)

Table 1. Material Characteristics of Various Polyethylene Used in This Study

	LLDPE (3210)	m - LLDPE (5400)	m - LLDPE (5100)
density	0.920	0.916	0.920
MI	1.0	1.0	0.85
T_m (°C)	119.0	122.5	121.5
M_n	39600	45300	54000
M_w	192800	178700	184000
MWD	4.87	3.94	3.42
co - monomer	1 - butene	1 - octene	1 - octene
branch number/1000 C	17.87	17.4	15.2
wt%	6.9	12.6	11.1

haze
.¹¹ m - LLDPE
m - LLDPE
가
, branching
가

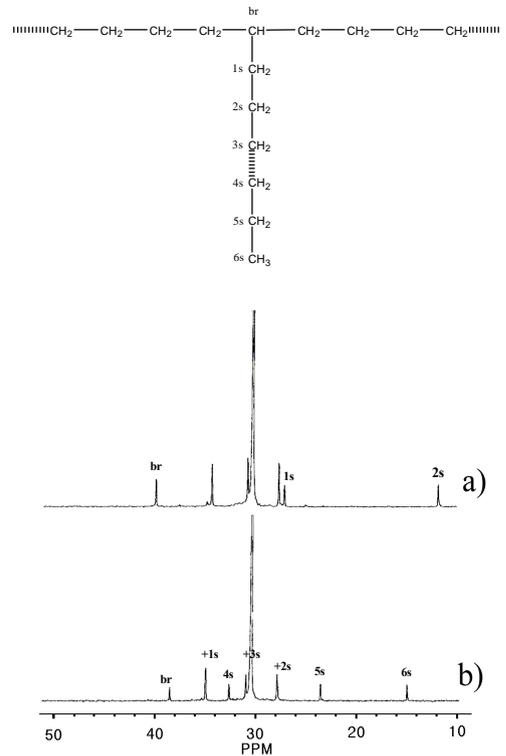


Figure 1. ¹³C NMR spectra for linear low density polyethylene : (a) LLDPE and (b) m - LLDPE 5400.

branching
Table 1
Table 1 chain branching number
Bruker ¹³C NMR(AC - 300)
TCB/benzene - d₆ 110
Decoupling inverse gated
decoupling(BB:12H), pulse angle 90°, delay
time 30 sec, acquisition time 1 sec

200 scanning Figure 1
spectrum (1) m -
LLDPE long chain branching(LCB)
LLDPE short chain branching(SCB)

$$LCB = IA_{+1s} / 3IA_{tot} \quad (1)$$

IA_{+1s} chain branch, IA_{tot}
 m-LLDPE LLDPE
 632.8 nm He/
 Ne laser, detector 576 x 384
 pixel CCD detector cover
 glass cover glass

가 30 μm
 hot
 stage, 112 - 116

H_v pattern pattern 45°
 intensity 1 H_v profile
 (2) scattering vector q

$I(q)$ vs. q plotting
 scattering angle (θ_{max}) (3)
 (R_{Hv})

$$G(\mu\text{m}/\text{sec}) \quad (R_{Hv \max})$$

$$q = (4 / \lambda) \sin(\theta / 2) \quad (2)$$

$$4.09 = 4 (R_{Hv} / \lambda) \sin(\theta_{max} / 2) \quad (3)$$

induc-
 tion time intensity q
 invariant Q_{Hv}

$$Q_{Hv} = \int_0^\infty I(q)q^2 dq \quad (4)$$

Leitz
 Mettler hot stage FP - 82HT

graph

Figure 2 (a), (b) branching 가
 (3210)
 (5400) 116 H_v
 pattern

(four - leaf - clover)
 pattern 3

m - LLDPE
 5400 LLDPE

H_v pattern
 가 H_v pattern

Figure 2(c)
 branching 가 m - LLDPE 5400
 m - LLDPE 5100 m - LLDPE 5400
 H_v pattern
 LLDPE

Figure 3 116 H_v pattern
 45° intensity scattering angle
 intensity가 가
 scattering angle 가
 가

Scattering angle
 m - LLDPE 5100, LLDPE 3210 m - LLDPE
 5400 Figure 2

Figure 4 q $I(q)$ H_v pattern
 invariant Q Q
 가 , m - LLDPE 5400

invariant가 가 가
 LLDPE invariant가 가

, m - LLDPE 5100 LLDPE
 invariant가 가 H_v

pattern invariant

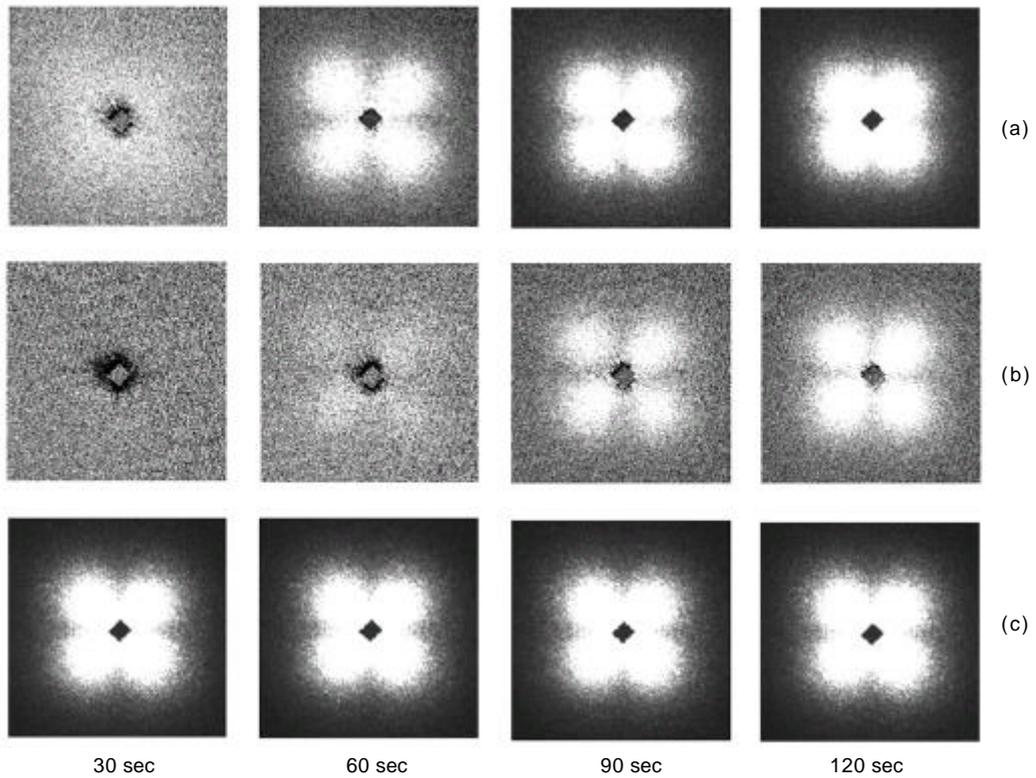


Figure 2. H_v light scattering patterns during the crystallization at $T_c=116$: (a) LLDPE, (b) m - LLDPE 5400, and (c) m - LLDPE 5100.

invariant Q 가
 invariant가
 induction time
 , induction time Gibbs free energy 가
 (embroy)
 m - LLDPE 5400
 LLDPE branching 가
 LLDPE embroy
 LLDPE 5400 LLDPE m -
 branching embroy
 m - LLDPE가 LLDPE
 가 embroy
 branching induction time
 branching 가
 m - LLDPE 5100 induction time
 embroy

branching branching
 . Table 1
 LLDPE 가 butene
 m - LLDPE 5400 octene
 long branching
 가
 octene
 . Figure
 m - LLDPE
 branching induction time
 branching 가
 m - LLDPE 5100 induction time
 embroy

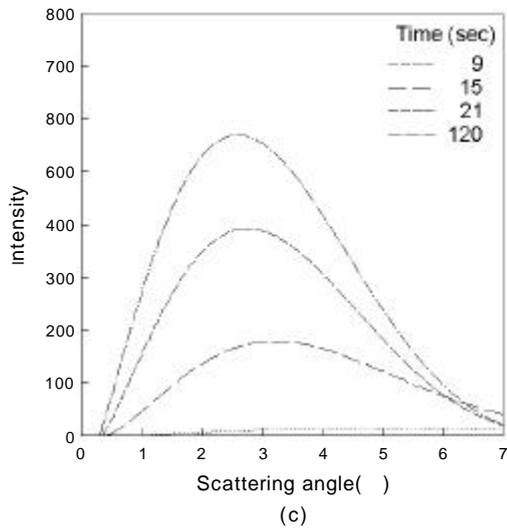
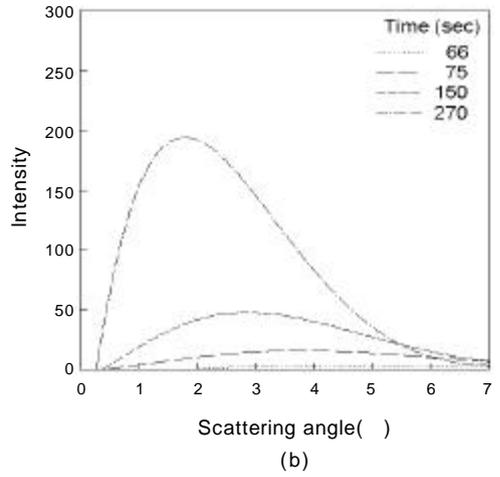
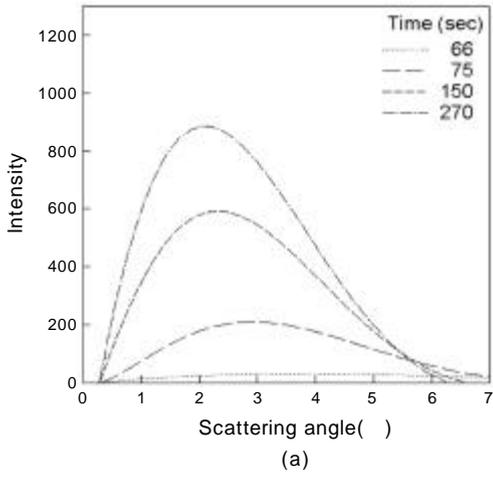


Figure 3. Scattering angle vs intensity $I(q)$ at $T_c=116$: (a) LLDPE, (b) m-LLDPE 5400, and (c) m-LLDPE 5100.

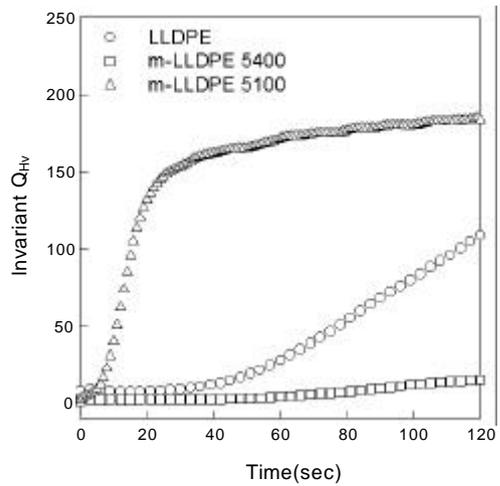


Figure 4. Time variation of the invariant Q_{Hv} at $T_c=116$.

branching
가
Figure 5
116
m-LLDPE 5400
가
m-LLDPE 5100
가
embroy
embroy가

branching
가
Figure 3
max
LLDPE
가
branching
가

LLDPE 5100
branching
가
Figure 6
Figure 5
G
branching
가

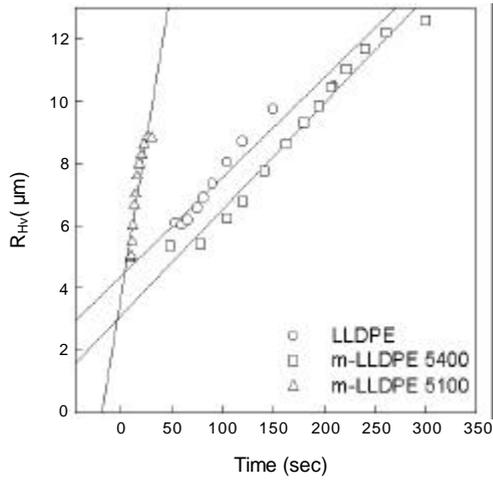


Figure 5. Time variation of the radius of the spherulites at $T_c=116$.

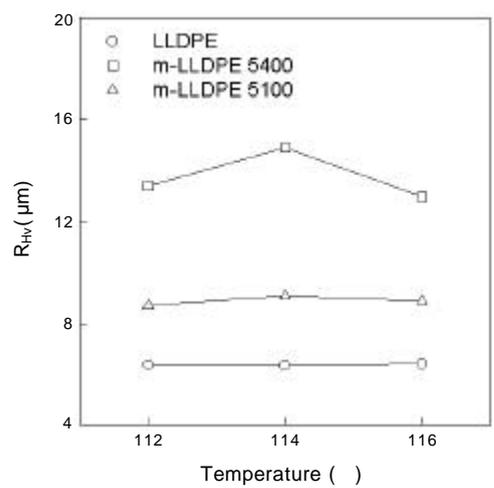


Figure 7. Maximum R_{HV} in various LLDPEs.

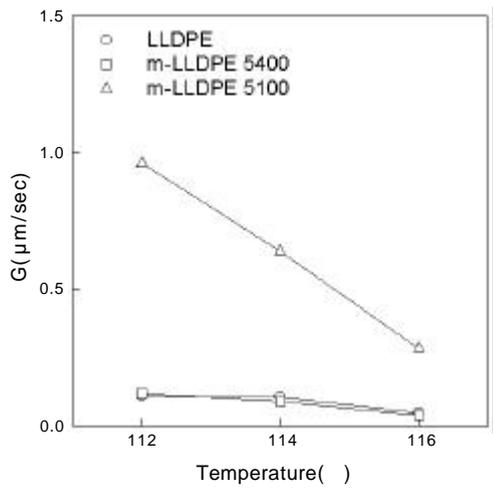


Figure 6. The growth rate of the spherulites in various LLDPEs.

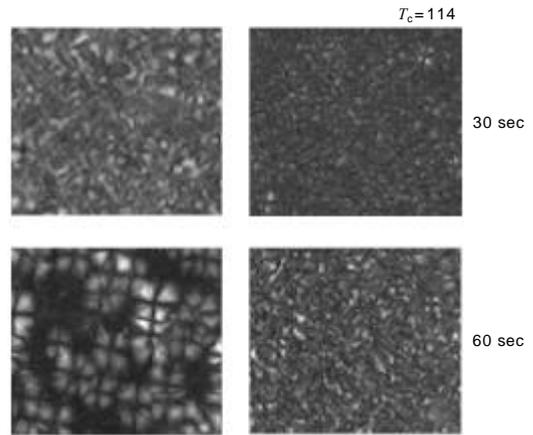


Figure 8. Polarized optical microphotography of LLDPEs at $T_c=114$: (a) m-LLDPE and (b) LLDPE.

branching 가 m-LLDPE 5400 LLDPE
branching 가 m-LLDPE 5100
가

, 가 가 가

Figure 7

m-LLDPE 5400 가 가

LLDPE
가 가 m-LLDPE 5100 가
112 - 116 가
Figure 8 hot
stage
microphotography
m-LLDPE가 LLDPE
가

Figure 6

m - LLDPE 5400 LLDPE
 induction time 가
 가
 LLDPE 5400
 가
 가

3. m - LLDPE
 가 LLDPE
 , m - LLDPE가 single site
 crystallites가
 : ¹³C NMR

crystallites가

가

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1.

embryo
 induction time branching
 octene
 m - LLDPE가 butene
 LLDPE induction time
 m - LLDPE branching 가
 induction time

2.

branching
 branching 가