Solubility of 1-Hexene in LLDPE Synthesized by (2-MeInd)$_2$ZrCl$_2$/MAO and by Mg(OEt)$_2$/DIBP/TiCl$_4$–TEA

HYOUNG-JOON JIN, SEWON KIM, JIN-SAN YOON

Department of Polymer Science and Engineering, Inha University, 402-751 Inchon, South Korea

ABSTRACT: The solubility of 1-hexene was measured for linear low-density polyethylenes (LLDPEs) produced over a heterogeneous Ziegler–Natta catalyst, Mg(OEt)$_2$/DIBP/TiCl$_4$–TEA (ZN), and over a homogeneous metallocene catalyst, (2-MeInd)$_2$ZrCl$_2$–MAO (MT). The 1-hexene solubility in LLDPEs was well represented by the Flory–Huggins equation with a constant value of χ. ZN–LLDPEs dissolved a larger amount of 1-hexene and thus showed a lower value of χ compared to MT–LLDPEs. The Flory–Huggins interaction parameter χ, or the solubility of 1-hexene at a given temperature and pressure, was suggested as a sensitive measure for the composition distribution of LLDPEs. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1566-1571, 2002; DOI 10.1002/app.10418

Key words: metallocene catalyst; Ziegler–Natta polymerization; copolymerization; gas permeation

INTRODUCTION

Linear low-density polyethylenes (LLDPEs) are produced commercially by Ziegler–Natta catalysts or by Philips catalysts. Both catalysts have multiple active sites and synthesize LLDPEs with broad molecular weight distributions.[1] The activity of the catalysts for ethylene is much higher than that for α-olefins, and the longer the α-olefins, the more difficult is the incorporation of the α-olefin units in the copolymers.[2,3] In addition, LLDPEs from the catalysts have a broad composition distribution, giving rise to bad odor, a large amount of extractables, poor heat seal properties, and so on.

A metallocene catalyst, bis-2-methylindenyl zirconium dichloride–methylaluminoxane [(2-MeInd)$_2$-ZrCl$_2$–MAO] (MT), produced LLDPEs with a narrower composition distribution compared to a heterogeneous Ziegler–Natta catalyst, magnesium diethoxide/diisobutyl phthalate/titanium tetrachloride–triethylaluminum [Mg(OEt)$_2$/DIBP/TICl$_4$–TEA] (ZN), in that LLDPEs from the latter catalyst had higher crystallinity, a higher melting point, and a broader DSC melting peak than those from the former catalyst, when the copolymers had a density similar to each other.[1]

The composition distribution of copolymers has usually been characterized using the temperature–rise–elution–fractionation (TREF) technique. However, this technique requires extensive labor and a tedious procedure.

In this study, LLDPEs, with densities in the range between 0.874 and 0.924, were prepared by ZN and MT catalysts using 1-hexene, 1-octene, and 1-octadecene as comonomers. The solubility of 1-hexene in LLDPEs having similar density was explored to investigate the dependence of the solubility on the copolymer composition distribution.

Table I Characteristics of LLDPEs

Catalyst Type	Code	Comonomer Type	Comonomer Content (mol %)	M_w ($\times 10^5$)	M_w/M_n	Density (g/cm^3)
Mg(OEt)$_2$/DIBP/TiCl$_4$–TEA	ZNH924	1-Hexene	3.5	2.43	4.09	0.924
	ZNO919	1-Octene	5.7	3.24	4.39	0.919
	ZNH918	1-Hexene	7.3	2.96	4.40	0.918
	ZNB905	1-Butene	—	2.32	5.58	0.905
	ZNB900	1-Butene	26.3	3.91	4.38	0.900
(2-MeInd)$_2$ZrCl$_2$/MAO	MTH923	1-Hexene	1.8	25.78	2.29	0.923
	MTH918	1-Hexene	3.5	23.23	2.54	0.918
	MTH912	1-Hexene	6.6	25.66	2.71	0.912
	MTH905	1-Hexene	8.7	23.01	2.63	0.905
	MTH894	1-Hexene	12.3	3.05	3.66	0.894
	MTH879	1-Hexene	20.8	2.17	2.72	0.879
	MTOD919	1-Octadecene	0.9	24.16	3.02	0.919
	MTOD915	1-Octadecene	1.8	24.61	2.76	0.915
	MTOD912	1-Octadecene	2.1	23.33	2.57	0.912
	MTOD904	1-Octadecene	2.3	20.18	2.58	0.904

EXPERIMENTAL

Copolymers of ethylene/1-butene, ethylene/1-hexene, and ethylene/1-octene were synthesized using the Ziegler–Natta catalyst, ZN, and copolymers of ethylene/1-hexene and ethylene/1-octadecene using the metallocene catalyst, MT. The polymerization and characterization methods of the copolymers were precisely described in our previous article.[4] Table I summarizes the characteristics of the LLDPEs obtained. Film specimens having a 0.1-mm thickness were prepared by pressing the polymerized powder on a hot press at 170°C under 275 psi for 5 min and subsequently under 690 psi for 1 min and finally quenching in ice water.

The crystallinity of copolymers has been defined as the ratio of the melting enthalpy of the DSC (Perkin–Elmer DSC 7) thermogram to that of a perfect polyethylene crystal (290 J/g).[5] The DSC thermogram was obtained for 7 mg of the sample film by scanning from room temperature to 160°C at a rate of 10°C/min.

The solubility was measured by monitoring the extension of a quartz spring (0.5 mm/mg of modulus) due to the weight variation accompanied by the sorption.[6] The sorption chamber was kept under a vacuum at the sorption temperature until all the volatile substances were removed from the sample to attain a constant weight. The 1-hexene vapor was introduced into the sorption chamber

from a hot water-jacketed evaporator. The airtight valve connecting the sorption chamber and the evaporator was closed and the weight gain was followed with a cathethometer having a 10-μm precision. Equilibrium solubility was determined when the weight ceased to increase for
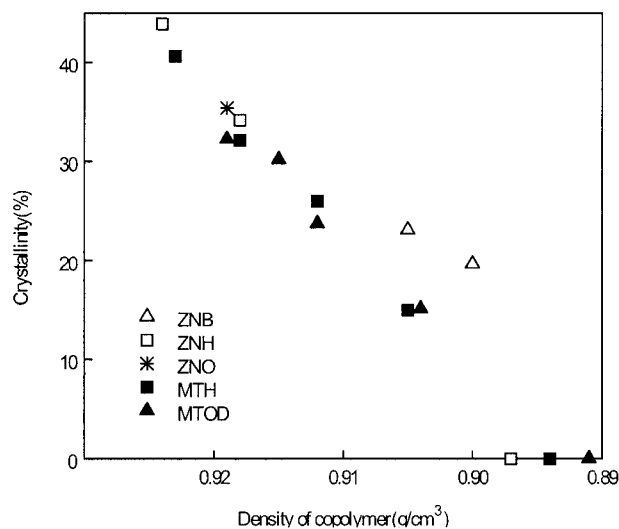

Figure 1 Crystallinity of LLDPEs as a function of density. LLDPEs were produced by copolymerizing ethylene with 1-butene (B), 1-hexene (H), 1-octene (O), or 1-octadecene (OD) over the heterogeneous Ziegler–Natta catalyst (ZN) or over the metallocene catalyst (MT).

Table II.   Solubility of 1-Hexene ($\times 10^{-3}$ g/g) in LLDPEs Based on Unit Weight of the Copolymers

	Temperature											
	70°C				60°C				50°C			
	Pressure											
LLDPE	0.1 atm	0.2 atm	0.3 atm	0.4 atm	0.1 atm	0.2 atm	0.3 atm	0.4 atm	0.1 atm	0.2 atm	0.3 atm	0.4 atm
ZNH924	6.38	11.31	17.98	26.04	7.78	13.88	22.3	33.08	9.87	21.43	35.38	51.65
ZNH918	6.81	12.52	20.04	29.53	8.56	15.93	26.54	39.52	11.09	24.07	39.58	58.9
ZNB905	9.71	19.08	29.03	42.27	11.95	24.33	40.1	57.6	16.72	32.94	56.06	92.78
ZNB900	10.21	20.18	30.86	45.33	13.01	26.39	44.3	64.04	17.52	35.15	61.28	100.53
ZNO919	7.87	13.19	20.98	30.95	9.21	17.38	27.8	40.1	12.99	26.05	42.30	61.45
MTH923	5.24	10.32	16.83	25.12	6.29	12.61	21.05	32.04	8.55	18.05	30.51	46.62
MTH918	5.6	11.67	18.49	26.89	7.83	14.27	23.7	35.55	9.65	19	32.65	49.13
MTH912	8.36	15.66	24.56	35.2	9.42	19.18	33.52	51.52	13.08	24.51	42.16	62.32
MTH905	12.02	20.56	31.5	44.35	13.69	25.44	45.45	67.6	17.98	35.9	59.28	90.60
MTH894	13.47	27.42	44.58	61.34	17.05	37.75	60.33	89.9	21.53	48.72	83.35	127.6
MTH879	15.65	31.73	49.59	72.03	18.55	43.13	72.72	107.12	31.78	58.03	100.87	165.48
MTOD919	5.85	12.28	19.19	27.67	8.44	15.48	24.48	36.73	10.4	19.85	34.66	50.38
MTOD915	7.24	14.18	22.02	32.98	9.18	18.3	28.49	44.51	12.03	22.4	38.28	57.8
MTOD912	9.76	18.23	27.14	40.43	10.79	21.82	38.7	54.7	14.8	28.26	47.35	68.29
MTOD904	13.13	23.25	35.63	52.48	14.3	29.31	51.09	75.14	19.25	40.25	68.06	105.31

more than 8 h and the equilibrium of the vapor was read from a hot water-jacketed mercury manometer to avoid condensation of the vapor.

RESULTS AND DISCUSSION

Solubilization of a volatile solute in a semicrystalline polymer depends largely on the crystallinity of the polymer. Due to strong interactions between polymer molecules in the crystalline region, solubilization of the volatile solute in a semicrystalline polymer takes place mostly in the amorphous region.[7]

The crystallinity of the LLDPEs, determined from the melting endothermal enthalpy on the DSC thermogram, is plotted as a function of the density. The results are shown in Figure 1. It can been seen that the crystallinity decreased with decrease in the density of the copolymers. The crystallinity of LLDPEs synthesized by a heterogeneous Ziegler–Natta catalyst, ZN–LLDPE, was higher than that of LLDPEs from a homogeneous metallocene catalyst, MT–LLDPE, at a given copolymer density. The difference became more pronounced as the copolymer density decreased. MT

catalysts produce LLDPEs having a narrow molecular weight distribution and a narrow copolymer composition distribution. In contrast, ZN–LLDPEs possess a broad molecular weight distribution and a broad copolymer composition distribution.

It is generally accepted that the copolymer composition distribution becomes broader as the side-chain length of the incorporated α-olefin units becomes longer. The role of the α-olefin units in the copolymers is to obstruct the interactions between the copolymer molecules by formation of short-chain branches to reduce their crystallinity and, thus, their density.

In the LLDPEs with a broad composition distribution, the larger the copolymer molecules, the fewer the α-olefin units incoporated. Hence, the crystallization of the long copolymer molecules could persist until the average content of α-olefin units in the copolymer becomes high.

The solubility of 1-hexene in LLDPEs having a similar density was measured as a function of 1-hexene vapor pressure. The results are shown in Table II. ZN and MT signify that LLDPEs were produced over the heterogeneous Ziegler–Natta catalyst and over the metallocene catalyst, re-
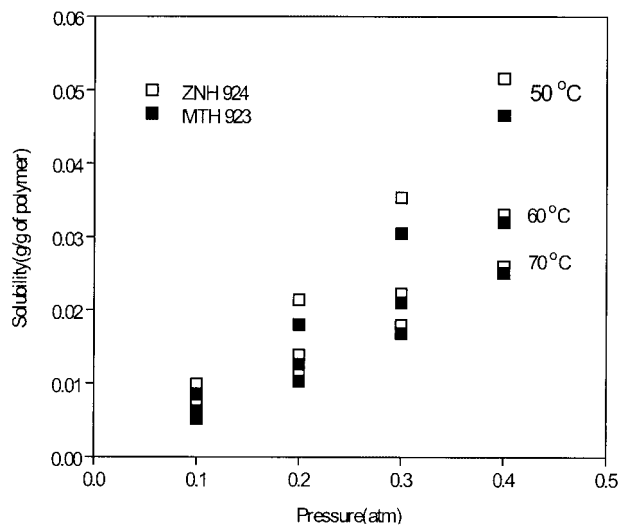
Figure 2 Solubility of 1-hexene (g/g of polymer) in ZNH924 and MTH923.

Figure 4 Solubility of 1-hexene (g/g of polymer) in ZNH918 and ZNO919.

spectively. The subsequent letters, B, H, O, and OD, mean that 1-butene, 1-hexene, 1-octene, and 1-octadecene were used as the comonomers, respectively. The number following the acronym corresponds to the copolymer density in kg/m^3.

A larger amount of 1-hexene was dissolved in ZNH924 than in MTH923 even though the latter had a lower density than the former (Fig. 2). In the same context, ZNH918 had higher 1-hexene solubility than that of MTH918 (Fig. 3). The dependence of the 1-hexene solubility on the copolymer composition distribution became more sig-
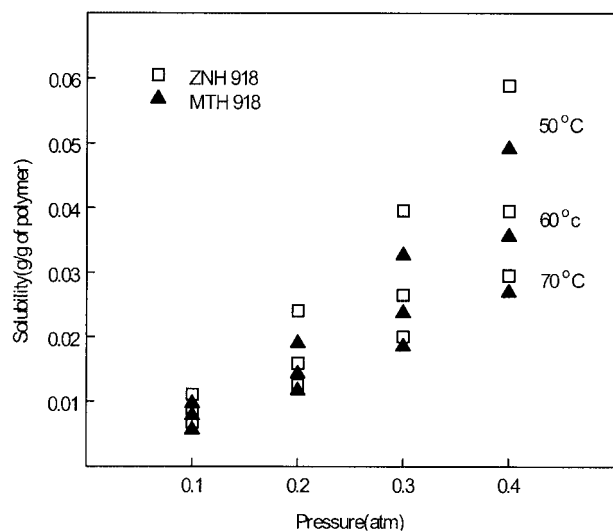
nificant as the measuring temperature was lowered and as the copolymer density was decreased.

The 1-hexene solubilities for ZNH, ZNO, MTH, and MTOD are compared in Figures 4 and 5. The 1-hexene solubility was higher in LLDPEs having longer α-olefin units. However, the solubility difference was not very marked. It is interesting to observe that the difference of the 1-hexene solubility at 50°C between ZNH918 and ZNO919 was more discernible than that between MTH918 and MTOD919, indicating that the effect of the α-olefin types on the copolymer composition distribu-

Figure 3 Solubility of 1-hexene (g/g of polymer) in ZNH918 and MTH918.

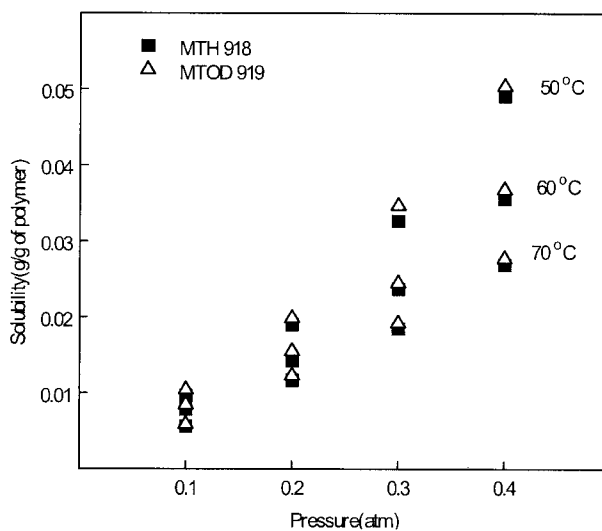**Figure 5** Solubility of 1-hexene (g/g of polymer) in MTH918 and MTO919.

Table III Solubility of 1-Hexene ($\times 10^{-3}$ g/g) in LLDPEs Based on Unit Weight of Amorphous Fraction of the Copolymers

	Temperature											
	70°C				60°C				50°C			
	Pressure											
LLDPE	0.1 atm	0.2 atm	0.3 atm	0.4 atm	0.1 atm	0.2 atm	0.3 atm	0.4 atm	0.1 atm	0.2 atm	0.3 atm	0.4 atm
ZNH924	11.38	20.17	32.06	46.43	13.88	24.75	39.75	58.97	17.6	38.21	63.08	92.09
ZNH918	10.35	19.02	30.44	44.84	13.00	24.19	40.30	60.01	16.83	36.55	60.1	89.45
ZNB905	12.63	24.82	37.76	54.98	15.54	31.64	52.16	74.92	21.75	42.84	72.91	120.69
ZNB900	12.70	25.12	38.42	56.42	16.20	32.84	55.14	79.71	21.8	43.76	76.28	125.13
ZNO919	12.18	20.41	32.46	47.89	14.24	26.90	43.01	62.06	20.11	40.31	65.47	95.10
MTH923	8.82	17.4	28.36	42.32	10.59	21.25	35.47	53.99	14.4	30.41	51.41	78.55
MTH918	8.25	17.19	27.24	39.60	11.54	21.01	34.91	52.37	14.22	27.98	48.08	72.37
MTH912	1.29	21.15	33.17	47.54	12.72	25.91	45.28	69.59	17.66	33.10	56.95	84.18
MTH905	14.14	24.19	37.05	52.17	16.11	29.92	53.46	79.52	21.15	42.23	69.73	106.58
MTH894	13.47	27.42	44.58	61.34	17.05	37.75	60.33	89.9	21.53	48.72	83.35	127.6
MTH879	15.65	31.73	49.59	72.03	18.55	43.13	72.72	107.12	31.78	58.03	100.87	165.48
MTOD919	8.63	18.12	28.31	40.83	12.45	22.84	36.12	54.19	15.35	29.29	51.15	74.34
MTOD915	10.38	20.30	31.54	47.23	13.14	26.21	40.81	63.74	17.22	32.08	54.83	82.78
MTOD912	12.79	23.90	35.59	53.02	14.15	28.62	50.75	71.73	19.40	37.06	62.09	89.55
MTOD904	15.47	27.38	41.97	61.82	16.85	34.53	60.19	88.52	22.67	47.42	80.17	124.06

tion was more significant for the ZN-catalyzed copolymerization system than for the MT-catalyzed one.

The solubility of a solute is probably negligible in the crystalline phase. The mobility of the polymer molecules seized by the crystalline phase are restricted so that the solute should be less solubilized in this domain than in the amorphous fraction. The 1-hexene solubility normalized with respect to the amount of the amorphous polymer in MT copolymers as well as in ZN ones increased as the copolymer density decreased (Table III). At present, it is not known whether this is due to a change in the composition distribution or due to the complex solubilization behavior of semicrystalline polymers.

Temperature–rise–elution–fractionation (TREF)[8,9] has been used for the characterization of the copolymer composition distribution, but this technique requires a tediously long procedure. DSC can be employed as a convenient means for indirect measurement of the composition distribution of the semi-crystalline copolymers. However, as shown in Figure 1, the difference of crystallinity between ZN–LLDPEs and MT–LLDPEs was not discernible when the copol-

ymer density was higher than 0.918. In comparison, the 1-hexene solubility detected the difference of the composition distribution of LLDPEs even when the copolymer density was as high as
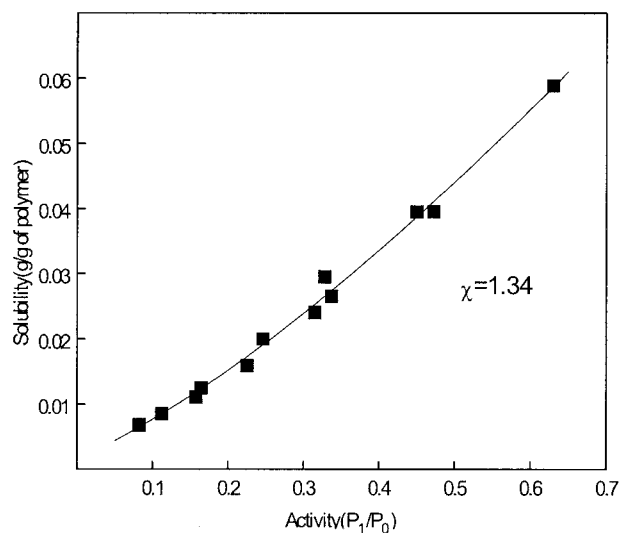

Figure 6 Representation of solubility of 1-hexene in ZNH918 by the Flory–Huggins equation with a constant value of χ.

Table IV   Apparent χ Values for Absorption of 1-Hexene in LLDPEs at 50°C

	Crystallinity (%)	Interaction Parameter (χ)
ZNH924	43.9	1.45
ZNO919	35.4	1.29
ZNH918	34.2	1.34
ZNB905	23.1	1.02
ZNB900	19.7	0.95
MTH923	40.7	1.53
MTH918	32.1	1.46
MTH912	26.0	1.21
MTH905	15.0	0.95
MTH894	0.0	0.69
MTH879	0.0	0.54
MTOD919	32.2	1.43
MTOD915	30.2	1.30
MTOD912	23.7	1.12
MTOD904	15.1	0.84

0.924, indicating that the solubility of volatile solutes could be a sensitive yardstick for the copolymer composition distribution.

The absorption behavior of a volatile solute in a polymer is represented by the Flory–Huggins theory as in eq. (1)[3]:

$$\ln(a_1) = \ln(\Phi_1) + (1 - \Phi_1) + \chi (1 - \Phi_1)^2 \quad (1)$$

where the activity of the solute, a_1, can be approximated to be the absorption pressure divided by the 1-hexene vapor pressure at the measurement temperature.

The Flory–Huggins interaction parameter, χ, usually depends not only on the temperature but also on the absorption pressure. However, the absorption of 1-hexene vapor in the LLDPEs is described quite well by eq. (1) with a constant value of χ, as exemplified in Figure 6, indicating that χ is a weak function of temperature and concentration. Berens[10] also observed that the Flory–Huggins equation fit well the solubility of vinyl chloride in poly(vinyl chloride) with a constant value of χ over a wide concentration range and a temperature range of 30–60°C. The 1-hexene vapor pressure was calculated from the Antoine equation with the values of the coefficients listed in Reid et al.'s book.[11]

χ values for the 1-hexene absorption in LLDPEs are summarized in Table IV. MT–LLDPEs had higher χ values compared to those of ZN–LLDPEs. Moreover, LLDPEs with 1-hexene showed higher χ values than those of LLDPEs with 1-octene or 1-octadecene as a comonomer.

Sehanobish et al.[12] claimed that side branches in an amorphous phase did not have any influence on the density of the amorphous region. However, it is to be noted that MH879 had a lower density than that of MH894 and that the χ value for MH879 was much lower than that for MH894, even though neither of the two copolymers showed any detectable melting peaks on the respective DSC thermograms. In conclusion, we suggest that the Flory–Huggins parameter χ or the solubility of 1-hexene at a given temperature and pressure are sensitive means for comparison of the composition distribution of LLDPEs of the same density.

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