

Sol-Gel Transition of Crystalline Polymer

Masaru Okabe

Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute
of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa, 243-0292, Japan
FAX: 046-242-8760 e-mail: okabe@chem.kanagawa-it.ac.jp

The crystalline junction size (ζ) of ethylene and 1-hexene copolymer gel was estimated from gel-melting temperatures using the theory derived by Takahashi, Nakamura, and Kagawa (TNK theory). The junction size was examined as a function of number of short-chain branching (SCB) as well as interaction parameter (χ_{12}) between polymer and solvent. The gel-melting temperature (T_m^g) increased logarithmically with increasing polymer concentration. A linear relationship was found between $1/T_m^g$ and $\ln(V_2N)$, where V_2 is the volume fraction of the copolymer and N is the weight-average degree of polymerization, suggesting that the TNK theory is applicable to T_m^g of LLDPE gel. The quantitative analysis by the TNK theory led to the result that the junction size ζ decreased with increasing SCB, and increased with increasing χ_{12} .

Key words: thermoreversible gel, ethylene/1-hexene copolymer, gel-melting temperature, polymer/solvent interaction parameter, junction size

1 INTRODUCTION

In previous studies, we reported that linear low-density polyethylene (LLDPE) in organic solvents formed thermoreversible gel from moderately concentrated solution without precipitating into crystalline phase[1-3]. Since LLDPE is a copolymer of ethylene and alkene such as 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene, the copolymer has various types of short-chain branchings(SCB). In the characterization of thermoreversible gel, it is very important to estimate the junction point size of gel. The junction size depends considerably on the kind of solvent for gelation as well as the number of SCB.

In this study, the junction point size (ζ) in number of consecutive ethylene units per crystalline sequence is estimated as a function of SCB using a copolymer of ethylene and 1-hexene. Moreover, relation between the junction size ζ and polymer/solvent interaction parameter (χ_{12}) is investigated.

2 EXPERIMENTAL

2.1 Materials

Four samples of unfractionated LLDPE, supplied by Japan Polyolefins Co., were used. Physical properties of the samples are listed in Table 1. The samples had nearly equal molecular weights (\bar{M}_w), but the number of SCB per 1000 methylenes (SCB/1000CH₂) was different. Each sample was dissolved in xylene above its boiling point, precipitated into cooled methanol, and dried under reduced pressure. Ethylcyclohexane (mp= -111°C; bp=130-132°C) was used as a solvent for gelation and purified by distillation before use.

2.2 Preparation of Gel and Gel-Melting Temperature

A gel was prepared in a sealed glass tube with ca. 35cm length and 1cm inner diameter by the following procedure: A definite weight of LLDPE and solvent (5cm³) together with a steel ball were placed in the glass tube and sealed. The sample was dissolved com-

Table1. Ethylene/1-hexene copolymers

Sample	$\bar{M}_w \times 10^{-4}$ ^{a)}	SCB/1000CH ₂ ^{b)}
S-1	8	5
S-2	8	20
S-3	8	24
S-6	8	28

a) \bar{M}_w , weight-average molecular weight determined by GPC.

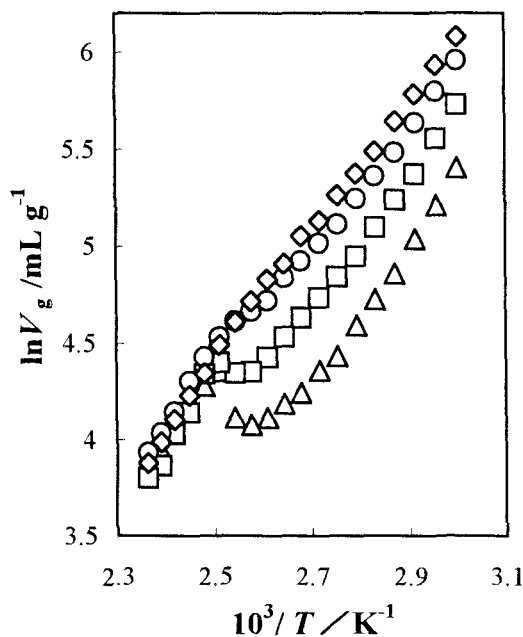
b) SCB/1000CH₂, number of short-chain branching per 1000CH₂.

pletely at 140-160°C. The glass tube was then immersed in a thermobath kept at 25°C, and maintained for 3h to make a gel. Gel-melting temperature was measured by the falling-ball method described previously, using a steel ball of ca. 30mg weight with 2mm diameter[4].

The gel was heated from 25°C at a rate of 6°C h⁻¹ while the height of the steel ball was recorded as a function of temperature.

2.3 Column Preparation and Measurement of Inverse Gas Chromatography (IGC)

A definite amount of LLDPE was dissolved in toluene and the solution was deposited on chromosorb. The solvent on chromosorb was evaporated by gentle stirring and heating. A solid support (chromosorb) coated with LLDPE was dried under reduced pressure at 50°C for 24h, and packed into a stainless steel column. An IGC experiment was carried out by using a GL Science GC-380 type gas chromatograph equipped with a flame ionization detector (FID). Helium gas was used as a carrier, while methane gas was used as a marker. The retention time (Δt) was determined from the difference between

Fig.1. Relation between $\ln V_g$ and $10^3/T$.

◇: S-6, ○: S-3, □: S-2, △: S-1

maximum peaks of marker and probe (solvent). The retention volume V_g was calculated using the following equation [5]:

$$V_g = \frac{\Delta t \cdot F \cdot (P_0 - P_w) \cdot (273.15)}{W \cdot P_0 \cdot T_r} \times \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (1)$$

with

$$\Delta t = t_p - t_M \quad (2)$$

where V_g [mL g⁻¹] is the retention volume, F [mL min⁻¹] is the flow rate of carrier gas, P_0 [mmHg] is the pressure of outlet, P_w [mmHg] is the vapor pressure of water at T_r , P_i [mmHg] is the pressure of inlet, W [g] is the weight of polymer, and T_r [K] is the room temperature. Relation between $\ln V_g$ and $10^3/T$ is shown in Fig.1. The logarithm of V_g increases with decreasing temperature.

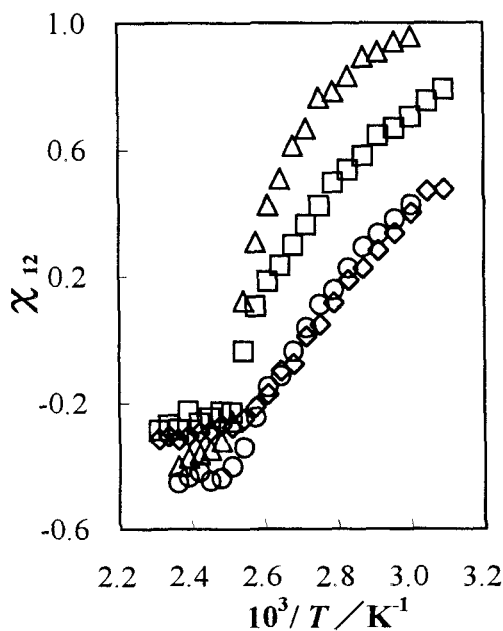
3 RESULTS AND DISCUSSION

3.1 Interaction Parameter

The Flory-Huggins interaction parameter χ_{12} can be obtained using the following equation[5]:

$$\chi_{12} = \ln \frac{(273.15) \cdot R \cdot V_2}{V_g \cdot V_1 \cdot P_1^0} - 1 - \frac{P_1^0}{R \cdot T} (B_{11} - V_1) \quad (3)$$

where V_1 [mL mol⁻¹] is the molar volume of probe, P_1^0 [mmHg] is the vapor pressure of probe, V_2 [mL g⁻¹] is the specific volume of polymer at column temperature, and B_{11} is the second virial coefficient of probe at the gaseous state. The values of V_1 , P_1^0 , and B_{11} were calcu-

Fig.2. Relation between χ_{12} and $10^3/T$.

△: S-1, □: S-2, ○: S-3, ◇: S-6

lated using the method reported by Daubert and Danner [6]. The χ_{12} parameter thus obtained was plotted against $10^3/T$ as shown in Fig.2. The parameter χ_{12} increases with decreasing temperature for each polymer, and increases with decreasing SCB/1000CH₂.

3.2 Junction Point Size of Gel

The solution of LLDPE in ethylcyclohexane converted to thermoreversible gel from moderately concentrated solution on cooling. In a dilute solution, a gel was not formed but crystalline phase separation took place. In order to estimate the junction point size of LLDPE gel, the theory derived by Takahashi, Nakamura, and Kagawa (TNK theory) was applied to gel-melting temperatures of LLDPE gel. According to the TNK theory, the junction size ζ in number of repeating ethylene units is given by the following equation [7]:

$$1/T_m^g = A - B \cdot \ln(V_2 \cdot N) \quad (4)$$

with

$$A = \frac{\zeta}{\zeta \cdot \Delta h_u + \zeta \cdot B' \cdot V_A - 2 \cdot \sigma_{ec}} \times \left(\frac{\Delta h_u}{T_m^0} + \frac{R \cdot V_A}{V_1} - R \cdot \ln X_A \right) \quad (5)$$

$$B = \frac{R}{\zeta \cdot \Delta h_u + \zeta \cdot B' \cdot V_A - 2 \cdot \sigma_{ec}} \quad (6)$$

where T_m^g [K] is the gel-melting temperature, ζ is the size of crystalline junction in number of ethylene units, Δh_u [cal mol⁻¹] is the heat of fusion of an ethylene unit, B' [cal cm⁻³] is the cohesive energy density defined by

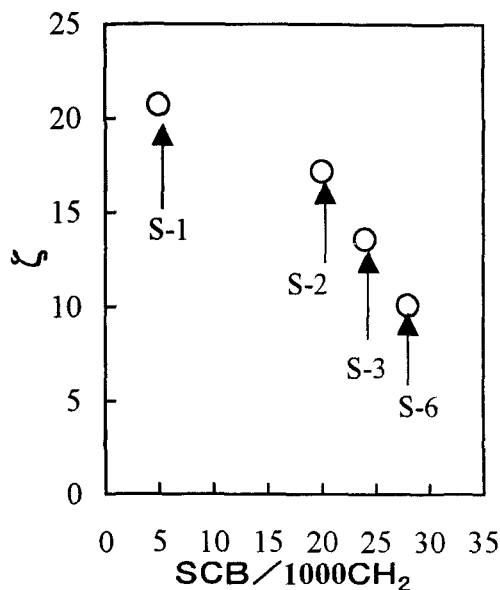


Fig.3. Relation between crystalline junction size ζ and number of short-chain branching SCB/1000CH₂.

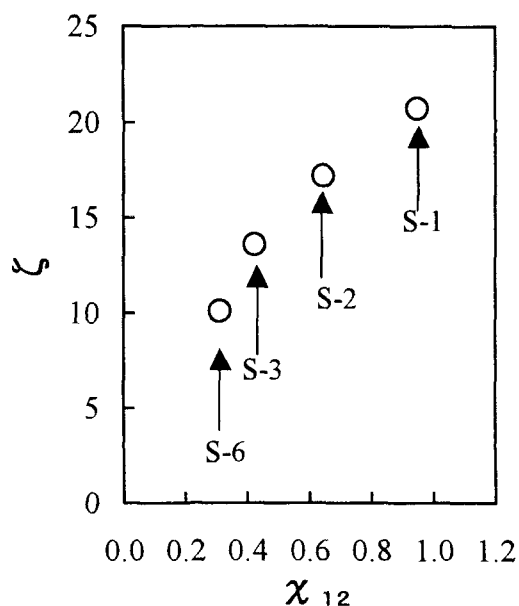


Fig.4. Relation between crystalline junction size ζ and Flory-Huggins interaction parameter χ_{12} measured at 60°C.

$\chi = B'V_1/RT$ (χ is the Flory-Huggins interaction parameter between polymer and solvent), V_1 and V_A [cm³ mol⁻¹] are the molar volumes of solvent and crystalline unit, respectively, σ_{ec} [cal mol⁻¹] is the end interfacial free energy per crystalline sequence, X_A is the mole fraction of crystalline units, T_m^0 [K] is the equilibrium melting temperature of polyethylene, R [cal mol⁻¹ K⁻¹] is the gas constant ($R=1.987$ cal mol⁻¹ K⁻¹), V_2 is the volume fraction of polymer in gel, and N is the weight-average degree of polymerization of LLDPE sample.

As the TNK theory includes two unknown parameters, i.e., ζ and σ_{ec} , these parameters can not be determined directly from eq.(4). So, the following procedure was taken in order to estimate the value of ζ : The intercept A and slope B given by eqs.(5) and (6) were determined experimentally by plotting $1/T_m^e$ against $\ln(V_2 \cdot N)$ according to eq.(4). While, the parameter ζ is written as follows, from eqs.(5) and (6):

$$\zeta = \frac{A}{B} \cdot \frac{R}{\Delta h_u / T_m^0 + R \cdot V_A / V_1 - R \cdot \ln X_A} \quad (7)$$

The junction point size ζ was determined from eq.(7) using the following numerical values [8]: $\Delta h_u=1920$ cal mol⁻¹; $V_A=28$ cm³ mol⁻¹; and $T_m^0=418.6$ K.

Plots of the size ζ vs. number of short-chain branching SCB/1000CH₂, and of ζ vs. interaction parameter χ_{12} are shown in Fig.3 and Fig.4, respectively. The data in Fig.3 shows that the junction point size ζ of LLDPE gel becomes smaller with increasing number of short-chain branching. Moreover, according to the data in Fig.4, the junction size ζ becomes larger when the gel was prepared in a poor solvent.

4 CONCLUSIONS

The present study clarifies the following results for the junction point size of ethylene/1-hexene copolymer gel in ethylcyclohexane:

1. The Flory-Huggins interaction parameter between the copolymer and solvent increases with decreasing number of short-chain (butyl) branching.
2. The crystalline junction size ζ in number of ethylene units becomes smaller with increasing number of butyl branching, and becomes larger in a poor solvent.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Yoshihiro Motegi of the Kawasaki Laboratory, Japan Polyolefins Co. for supplying the LLDPE samples and making their characterization. Partial support was obtained through the Grant-in-Aid from the Ministry of Education under grant number 12650891.

REFERENCES

- [1] M.Okabe, M.Isayama, and H.Matsuda, *J. Appl. Polym. Sci.*, **30**, 4735–4743(1985).
- [2] M.Okabe, M.Isayama, and H.Matsuda, *Polym. J.*, **17**, 369–376(1985).
- [3] M.Okabe, K.Mitsui, F.Sasai, and H.Matsuda, *Polym. J.*, **21**, 313–328(1989).
- [4] M.Okabe and H.Matsuda, *Kobunshi Ronbunshu*, **42**, 397–404(1985).
- [5] J.R.Conder and C.L.Young, "Physicochemical Measurement by Gas Chromatography", Wiley, New York, N.Y. (1979), pp.26–32, pp.190–192.

- [6] T.E.Daubert and R.P.Danner, ed., “*Physical and Thermodynamic Properties of Pure Chemicals*”, data compilation, Hemisphere Publishing, Corp., New York (1989).
- [7] A.Takahashi, T.Nakamura, and I.Kagawa, *Polym. J.*, **3**, 207–216(1972).
- [8] A.Takahashi, M.Sakai, and T.Kato, *Polym. J.*, **12**, 335–341(1980).

(Received December 8, 2000; Accepted March 26, 2001)