

Phenomenological Study on Sol-Gel Transition of Linear Low Density Polyethylene in Organic Solvents

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Synopsis

Solutions of linear low density polyethylenes in organic solvents formed thermoreversible gels on cooling. Gel-melting temperatures of the polymers in tetralin, decalin, and *o*-xylene were measured. They increased slowly with increasing polymer concentration. Experimental data were analyzed by the thermodynamic theory of Takahashi, Nakamura, and Kagawa, which is derived for the gel-melting temperature of a crystalline linear copolymer gel. A plot of the gel-melting temperature by the theory depended considerably on the kind of comonomer of the polymer.

INTRODUCTION

Sol-gel transition of crystalline copolymer or crystalline polymer with copolymeric character in a solvent is a well-known phenomenon.¹ In the previous papers,²⁻⁵ we reported that a branched low density polyethylene, which was considered as a crystalline copolymer, formed thermoreversible gel in tetralin, decalin, *o*-xylene, toluene, benzene, and cyclohexane-carbon disulfide mixed solvent with cooling and the gel converted to solution with warming. In these studies, the dependence of gel-melting temperature on polymer concentration and molecular weight was investigated and thermodynamic analysis was carried out by the theory of Takahashi, Sakai, and Kato,⁶ which was proposed for the gel-melting temperature of a crystalline copolymer.

Recently, Edwards and Mandelkern reported that a linear low density polyethylene in *p*-xylene, which was a copolymer of ethylene and 1-butene, converted to gel from its dilute solution.⁷ Independently, we have reported sol-gel transitions of linear low density polyethylenes in organic solvents.⁸⁻¹⁰ However, the nature or mechanism of gelation has not been fully clarified yet. Moreover, there is little theory for interpreting completely the gel-melting temperature of a polyolefin gel in organic solvents.

So, in this study, we measured the gel-melting temperatures of linear low density polyethylene gels formed in tetralin, decalin, and *o*-xylene, and applied the theory of Takahashi, Nakamura, and Kagawa¹ to the experimental results of gel-melting temperature in order to examine the depen-

dence of gel-melting temperature on the kind of comonomer of the polymer or the size of a crystallite in the gel.

EXPERIMENTAL

Materials

Seven samples of unfractionated linear low density polyethylene (LLDPE) were used for measurements of gel-melting temperature. Solvents were tetralin, decalin, and *o*-xylene. Typical physical properties of the samples are shown in Table I. Linear low density polyethylene is a copolymer of ethylene and alkene, and the comonomers of LLDPE-3-4, LLDPE-5-6, and LLDPE-9-11 are 1-butene, 4-methyl-1-pentene, and 1-octene, respectively. Each sample has a different number of short chain branches per 1000 methylene groups (SCB/1000 CH₂) and molecular weight.

Purification of a LLDPE sample was carried out as follows: Pellets of the sample were dissolved completely in purified xylene at its boiling point in a flask with a reflux condenser. The solution was then poured into cooled methanol with stirring. After washing with purified methanol, the sample was dried under reduced pressure at 70°C until a constant weight was reached. The solvents were purified by the ordinary method before use.

Measurement of Gel-Melting Temperature

The gel-melting temperature was measured by the so-called falling-ball method using a small steel ball and a glass tube. Schematic drawing of an apparatus for gel-melting temperature and the size of the glass tube are shown in Figure 1. The dependence of gel-melting temperature on the weight of a steel ball was examined preliminarily in our previous study,⁴ and about 30 mg weight with 2 mm in diameter of a steel ball was used for measurement of gel-melting temperature.

The LLDPE gel was formed in a glass tube as follows: A definite weight of sample, a definite volume of solvent, and a steel ball were placed in the glass tube, and it was sealed. The steel ball was then fixed at the upper

TABLE I
Typical Physical Properties of Linear Low Density Polyethylenes

Sample	Density (g/cm ³)	$M_w \times 10^{-4a}$ (GPC)	Comonomer	SCB/1000 CH ₂ ^b (NMR)
LLDPE-3	0.930	7.1	1-Butene	21.0
LLDPE-4	0.918	5.5	1-Butene	22.5
LLDPE-5	0.916	8.0	4-Methyl-1-pentene	15.3
LLDPE-6	0.923	8.4	4-Methyl-1-pentene	10.1
LLDPE-9	0.917	11.9	1-Octene	15.4
LLDPE-10	0.913	8.0	1-Octene	23.9
LLDPE-11	0.923	9.0	1-Octene	11.9

^a M_w , the weight-average molecular weight determined by GPC.

^b SCB/1000 CH₂, the number of short chain branches per 1000 methylene groups determined by ¹³C-NMR.

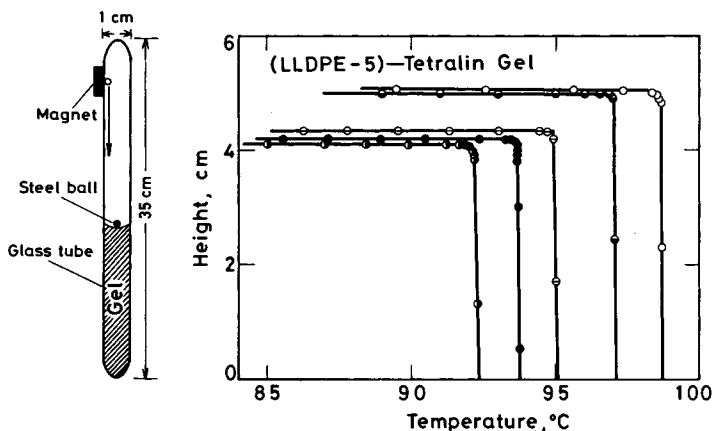


Fig. 1. Schematic drawing of an apparatus for gel-melting temperature and typical examples for measurement of gel-melting temperature by the falling-ball method: Concn ($\text{g}/100 \text{ cm}^3$): (●) 4.74; (●) 5.63; (⊖) 6.50; (⊙) 9.02; (○) 12.14.

part of the glass tube by a magnet. In tetralin and decalin, the polymer was dissolved completely at 180°C , and in *o*-xylene at 110°C . After the solution of LLDPE was maintained at room temperature for 5 min, the glass tube was immersed in a thermobath kept at 100°C for 25 min. Finally, the glass tube was immersed in a thermobath regulated at 10°C for 16 h to make a gel. During this process, phase separation did not occur, but a solution turned into a gel. After the solution converted to gel, the steel ball was carefully moved on the top of the gel by magnetic manipulation and the gel was warmed very slowly at a rate of $6^\circ\text{C}/\text{h}$. The height of the steel ball from a reference level was recorded at selected temperatures using a cathetometer. When the gel melted, the steel ball began to fall downwards.

Typical examples for measurement of gel-melting temperature are shown in Figure 1. The temperature at which the horizontal and vertical straight lines intersected was taken as the gel-melting temperature. The measurements were repeated five or six times at each concentration, and an average value was used for subsequent analysis of the gel-melting temperature.

RESULTS AND DISCUSSION

The solutions of LLDPE in tetralin, decalin, and *o*-xylene formed thermoreversible gels on cooling without precipitating into crystalline phase, whose concentrations were higher than about $4 \text{ g}/100 \text{ cm}^3$. In lower concentration region than about $4 \text{ g}/100 \text{ cm}^3$, the solution did not convert to gel by the method shown in the experimental section and the polymer precipitated from the solution with cooling.

Examples of relation between the gel-melting temperature T_m^g ($^\circ\text{C}$) and polymer concentration C ($\text{g}/100 \text{ cm}^3$) for tetralin system are shown in Figure 2. Similar relations were also obtained in other solvents. It is seen from Figure 2 that the gel-melting temperatures increase slowly with increasing polymer concentration, and these tendencies were similar to those of branched low density polyethylene gels reported in the previous paper.⁴

When a LLDPE solution converted to a gel, the gel exhibited considerable

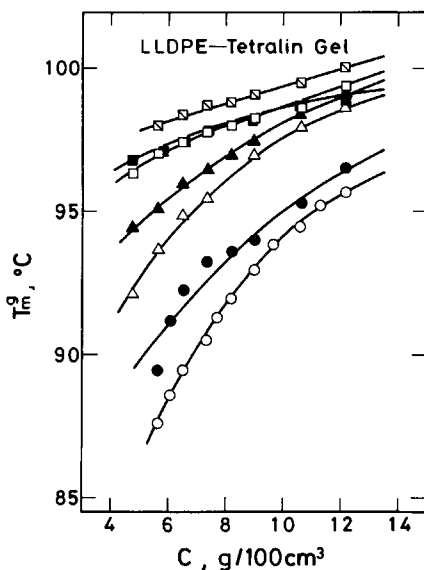


Fig. 2. Relation between the gel-melting temperature T_m^g and polymer concentration C for tetralin system. (●)LLDPE-3; (○)LLDPE-4; (△)LLDPE-5; (▲)LLDPE-6; (□)LLDPE-9; (◻)LLDPE-10; (◼)LLDPE-11.

turbidity. Therefore, the gel may include many small crystallites, and it may be seen that the crystallites behave as crosslinking junctions in the gel. Recently, Edwards and Mandelkern reported that the crystallite involved in a LLDPE gel formed in *p*-xylene was not a fringed micellar type, but a lamella structure from measurements of small-angle X-ray scattering.⁷ In this study, we also examined the structure of crystallite in the present LLDPE gel by a polarizing microscope. An example of polarizing micrograph of crystallite in (LLDPE-9) — tetralin gel is shown in Figure 3. In this photograph, many spherulites were observed. Similar photographs were also obtained for other LLDPE gels. Accordingly, it was found that the LLDPE gel included the spherulite, indicating the crystallites in the gel to be composed of lamella.

Taking into account a copolymeric character of crystalline linear polymer, Takahashi, Nakamura, and Kagawa¹ derived the thermodynamic theory for the gel-melting temperature of the polymer from the melting point depression of a copolymer-diluent system as formulated by Flory.¹¹ The details should be referred to the original paper.¹ The theory is written simply as follows:

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

with

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

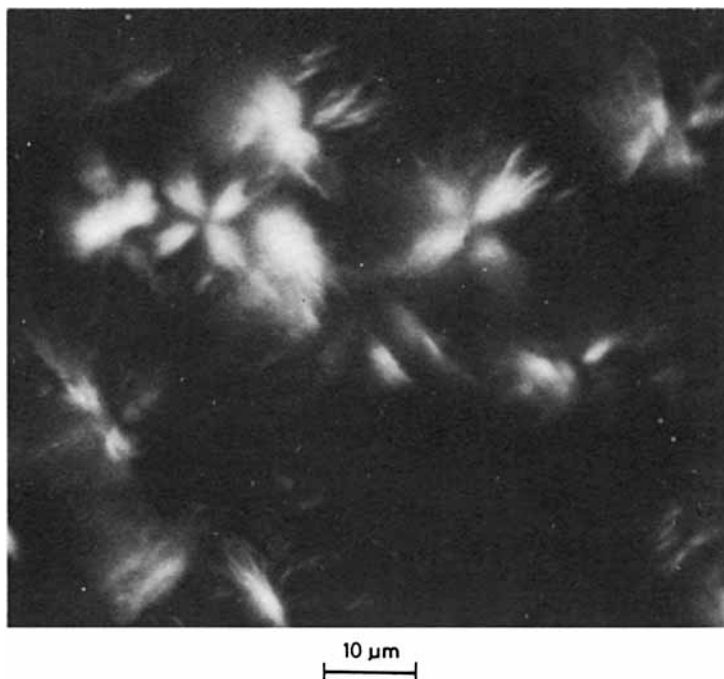


Fig. 3. Example of photograph of spherulite in LLDPE gel by polarizing microscope with crossed nicols: sample, LLDPE-9; comonomer, 1-octene; molecular weight, $M_w = 11.9 \times 10^4$; solvent, tetralin; concentration, $C = 5.63 \text{ g}/100 \text{ cm}^3$.

$$B = \frac{R}{\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec}} \quad (3)$$

where T_m^g is the observed gel-melting temperature of a linear crystalline copolymer gel, ζ the ethylene-unit length in a crystallite, Δh_u the heat of fusion of an ethylene unit, B' the cohesive energy density defined by $\chi_1 = B' V_1/RT$, χ_1 the interaction parameter between polymer and solvent, V_1 and V_A the molar volumes of solvent and a crystalline unit, respectively, σ_{ec} the end interfacial free energy per crystalline sequence, T_m^0 the melting temperature of polymer, R the gas constant, X_A the mole fraction of crystalline units, V_2 the volume fraction of the polymer in the gel, and N the weight-average degree of polymerization.

According to eq. (1), a plot of $1/T_m^g$ vs. $\ln V_2 N$ should yield a straight line, and, if the values of Δh_u , B' , X_A , and T_m^0 in eqs. (2) and (3) are known, ζ and σ_{ec} can be estimated from a intercept A and a gradient B of the straight line. First, we must confirm the linearity between $1/T_m^g$ and $\ln V_2 N$ for the gel-melting temperatures obtained for the present LLDPE gels. The plots of $1/T_m^g$ vs. $\ln \bar{V}_2 N$ are illustrated in Figures 4-6. In each solvent, three straight lines were obtained, depending exceedingly on the kinds of comonomer of the sample. Thus, it may be seen that the theory of Takahashi, Nakamura, and Kagawa is applicable to the gel-melting temperatures of LLDPE gels.

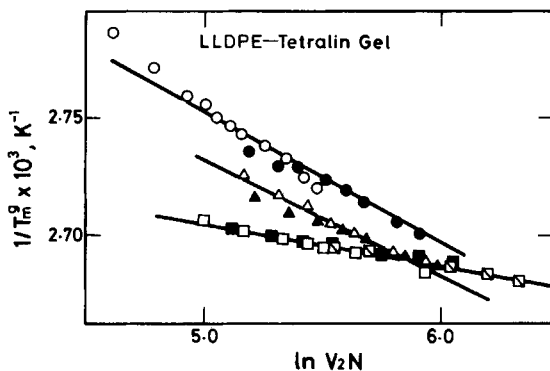


Fig. 4. Relation between $1/T_m^g$ and $\ln V_2N$ for tetralin system. (●)LLDPE-3; (○)LLDPE-4; (△)LLDPE-5; (▲)LLDPE-6; (◻)LLDPE-9; (◻)LLDPE-10; (■)LLDPE-11.

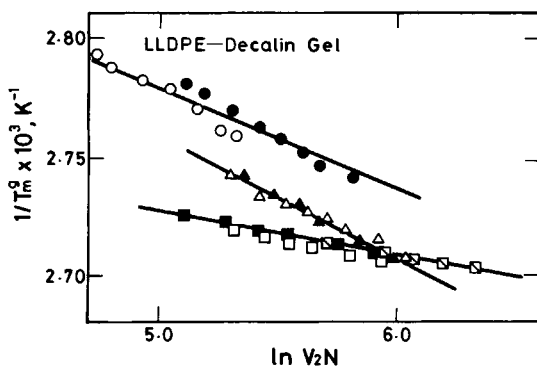


Fig. 5. Relation between $1/T_m^g$ and $\ln V_2N$ for decalin system. (●)LLDPE-3; (○)LLDPE-4; (△)LLDPE-5; (▲)LLDPE-6; (◻)LLDPE-9; (◻)LLDPE-10; (■)LLDPE-11.

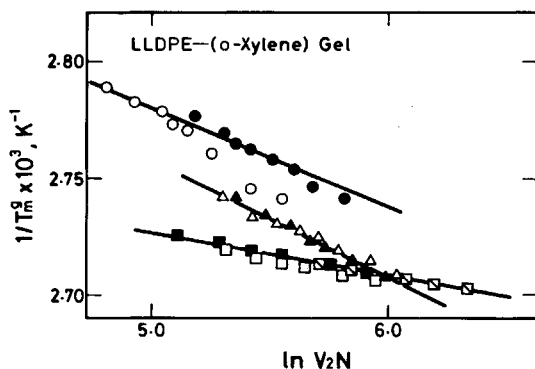


Fig. 6. Relation between $1/T_m^g$ and $\ln V_2N$ for *o*-xylene system. (●)LLDPE-3; (○)LLDPE-4; (△)LLDPE-5; (▲)LLDPE-6; (◻)LLDPE-9; (◻)LLDPE-10; (■)LLDPE-11.

In order to estimate the values of ζ and σ_{ec} by eq. (1), the interaction energy densities for the polymer-solvent pairs were determined by measurements of the swelling ratio as follows: 0.1 g of a linear low density polyethylene sample was molded into a film. The film was then irradiated by an electron beam for 60 Mrad so as to crosslink the polymer molecules. Soluble parts of the film were extracted by xylene at its boiling point in a soxhlet extractor for 24 h. The crosslinked film was dried under reduced pressure and its weight (W_0) was determined. Then, the crosslinked film was swollen in *p*-xylene at 72.7°C for 24 h and its weight (W_s) was measured. The swelling ratio Q_m was calculated by the equation

$$Q_m = \frac{1}{\Phi_2} = 1 + \frac{\rho_2}{\rho_1} \left(\frac{W_s - W_0}{W_0} \right) \quad (4)$$

where Φ_2 is the volume fraction of a polymer, ρ_1 and ρ_2 are the densities of a solvent and the polymer, respectively, and W_s and W_0 the weights of a swollen film and a dried film, respectively.

Using the value of swelling ratio Q_m calculated by eq. (4), the volume fraction Φ_2 of the polymer in the swollen film was determined by eq. (4). The molecular weight M_c between crosslinking points was calculated by Flory's equation¹² with the value of Φ_2 ,

$$M_c = \frac{M_n d V_0 (\Phi_2^{1/3} - 2\Phi_2/\nu)}{2dV_0(\Phi_2^{1/3} - 2\Phi_2/\nu) - M_n [\ln(1 - \Phi_2) + \Phi_2 + \chi_1 \Phi_2^2]} \quad (5)$$

where M_n is the number-average molecular weight of the sample before crosslinking, d the density of the film, V_0 the molar volume of the solvent, ν the functionality of a crosslinked point, and χ_1 the Flory-Huggins interaction parameter. With the numerical values of $\nu = 3$ and $\chi_1 = 0.511$ for polyethylene-(*p*-xylene) system, which were determined by Muthana and Mark,¹³ M_c was determined to be $M_c = 2.2 \times 10^3 - 4.7 \times 10^3$. Then, the same film was swollen in each solvent at 40°C for 24 h and the swelling ratio was determined. Finally, the χ_1 parameter for linear low density polyethylene in each solvent was calculated by eq. (5) with the value of M_c .

The molar volumes V_1 of solvents were calculated from the densities of the solvents, and the cohesive energy densities B' were determined from the swelling ratios of the polymer in the respective solvents. The mole fraction X_A of crystalline units was calculated from $X_A = [1 - 0.001(\text{SCB}/1000 \text{ CH}_2)]$, where SCB/1000 CH₂ is the number of short chain branches per 1000 methylene groups. Using the numerical values of $\Delta h_u = 1920$ cal/mol, $T_m^0 = 418.6$ K, and $V_A = 28$ cm³/mol, which were proposed by Takahashi et al.,⁶ the ethylene unit length in a crystallite ζ and the end interfacial free energy per crystalline sequence σ_{ec} were estimated, and these values are summarized in Table II.

It may be seen in Table II that the estimated values of ζ and σ_{ec} of LLDPE-9-11, whose comonomers are 1-octene, are the largest among the

TABLE II
Estimated values of ζ^a and σ_{ec}^b for LLDPE gels

Sample	Tetralin		Decalin		o-Xylene	
	ζ	σ_{ec} (cal/mol)	ζ	σ_{ec} (cal/mol)	ζ	σ_{ec} (cal/mol)
LLDPE-3	25.9	3930	26.3	4360	19.9	3650
LLDPE-4	17.7	3310	16.9	3420	16.5	3280
LLDPE-5	24.4	3770	29.6	4600	27.7	4220
LLDPE-6	31.2	4270	39.4	5390	21.2	3750
LLDPE-9	62.5	6300	42.1	5390	64.2	6810
LLDPE-10	50.0	5280	33.6	4570	53.1	5780
LLDPE-11	72.5	7110	40.5	5300	58.8	6500

^a ζ , ethylene unit length in a crystallite.

^b σ_{ec} , end interfacial free energy per crystalline sequence.

samples having different kinds of comonomer, that is, among LLDPE-3-4, LLDPE-5-6, and LLDPE-9-11, while these values of LLDPE-3-4 are the smallest, whose comonomers are 1-butene. These tendencies also correspond to the gel-melting temperatures shown in Figure 2. That is, the gel-melting temperatures T_m^g of LLDPE-9-11 are the highest, while T_m^g of LLDPE-3-4 are the lowest. Therefore, it is likely seen that the values of ζ and σ_{ec} of the LLDPE gels depend on the kinds of comonomer, and these values become larger when the branch length of comonomer becomes longer.

However, we have no assurance for validities of the values of ζ and σ_{ec} estimated in this study. These values should be compared with the values derived by other methods. Moreover, the present results were obtained by using unfractionated samples. Thus, the study also should be done with fractionated samples. These problems are left for future study. There is no theory for interpreting completely the gel-melting temperature of a polyolefin gel in which the spherulites exist. Consequently, a phenomenological treatment of the gel-melting temperature was carried out in this study using the theory of Takahashi, Nakamura, and Kagawa.

In conclusion, the following results were obtained for the sol-gel transition of linear low density polyethylene in organic solvents:

1. Linear low density polyethylenes in tetralin, decalin, and o-xylene convert to thermoreversible gels on cooling. The gel-melting temperature increases slowly with increasing polymer concentration.

2. Spherulites are observed in the gel, indicating the crystallites involved in the gel to be composed of lamella.

3. The gelation phenomenon of the polymer in organic solvents is a consequence of crystallization, and it is considered that the gel is thermodynamically composed of two phases: liquid (solution) phase and solid (crystallite) phase.

4. The theory of Takahashi, Nakamura, and Kagawa¹ is found to apply well to the systems studied, and the plot of $1/T_m^g$ vs. $\ln V_2N$ gave a common straight line, which was independent of the molecular weight of the polymer, when the comonomer of the polymer was identical. If the comonomer is different, another straight line was obtained.

5. Results of the present study suggest that the gel-melting temperature T_m^g and the size of a crystalline junction ζ depend considerably on the kind of comonomer of the polymer, and the values of T_m^g and ζ became larger when the branch length of comonomer became longer.

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