

Sol-Gel Transition of Branched Low Density Polyethylene in Organic Solvents

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(Received October 7, 1983)

ABSTRACT: The sol-gel transition of branched low density polyethylenes in decalin, tetralin, *o*-xylene, toluene and benzene was studied. Gel-melting temperatures increased with polymer concentration. Experimental data were analyzed by the theory proposed by Takahashi, Sakai, and Kato for the gel-melting temperature of branched polymers. Our data adhered closely to the theory by which the size of a crystalline junction in the gel could be estimated.

KEY WORDS Sol-Gel Transition / Gel / Gel-Melting Temperature / Polyethylene / Branched Polyethylene / Low Density Polyethylene /

In our previous papers,^{1,2} solutions of branched low density polyethylene in cyclohexane and carbon disulfide mixed solvents were shown to be converted to gels on cooling and that each such gel reverted to a solution on warming at near room temperature. The gel-melting temperature depended on the molecular weight of the polymer and solution concentration. At about that time, Takahashi, Sakai, and Kato³ proposed a theory for treating the gel-melting temperature of a branched polymer gel. This theory is useful for determining molecular weight dependence of the gel-melting temperature and estimating the size of a crystalline junction point in the gel. We applied this theory to gel-melting temperatures for a series of fractionated branched low density polyethylenes in cyclohexane and carbon disulfide mixed solvents.⁴ Recently, Barbam, Hill and Keller⁵ reported that a dilute solution of polyethylene in xylene was converted to gel on cooling, after it had been stirred at an elevated temperature. We also reported that solutions of branched low density polyethylene

in decalin, tetralin and *o*-xylene were converted to thermo-reversible gels on cooling.⁶

These facts indicate that the sol-gel transition of branched low density polyethylene in organic solvents is a general property of the polymer.

In this paper, sol-gel transitions of branched low density polyethylene in decalin, tetralin, *o*-xylene, toluene and benzene were studied and the experimental data obtained were analyzed by the theory of Takahashi, Sakai and Kato.

EXPERIMENTAL

Materials

The four samples used of unfractionated branched low density polyethylene were supplied and characterized by Motegi of the Ohita Laboratory, Showa Denko Co. Their typical physical properties are shown in Table I.

The samples, S-11, S-12, and S-14 had nearly equal numbers of branches per 1000 carbon atoms, but their molecular weights differed. The molecular weight and branching degree of

Table I. Physical properties of branched low density polyethylenes^a

| Sample | Density g cm ⁻³ | $M_w \times 10^{-4}$ (GPC) | CH ₃ /1000C (IR) | $[\eta]$ 100 cm ³ g ⁻¹ |
|--------|-------------------------------|-------------------------------|--------------------------------|---|
| S-11 | 0.921 | 7.4 | 24.2 | 0.875 |
| S-12 | 0.920 | 16.1 | 25.8 | 1.137 |
| S-14 | 0.923 | 13.7 | 24.2 | 1.099 |
| S-16 | 0.917 | 17.5 | 30.4 | 1.070 |

^a M_w , weight-average molecular weight obtained by GPC; CH₃/1000C, the number of methyl groups per 1000 carbon atoms determined by infrared analysis; $[\eta]$, measured in tetralin at 130°C.

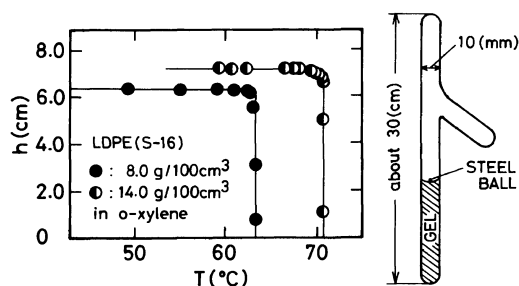


Figure 1. Gel-melting temperature apparatus and examples of gel-melting measurement.

S-16 were the largest among the samples examined. Each sample was dissolved in xylene at its boiling temperature, precipitated into cooled methanol, and dried under reduced pressure.

Decalin, tetralin, *o*-xylene, toluene and benzene were purified before use by ordinary methods.

Measurement of Gel-Melting Temperature

Gel-melting temperature was measured by the method proposed by Takahashi, Sakai and Kato³; for details, reference should be made to their papers.^{3,6} The apparatus for gel-melting temperature measurement is shown in Figure 1. A definite sample weight and a volume of the solvent were placed in the apparatus which

was then sealed. A steel ball about 30 mg in weight was placed in the arm of the apparatus. The polymer was dissolved completely at 110°C. After the solution had been maintained at room temperature for 10 min, the apparatus was immersed for 24 h in a thermobath regulated at 10°C. During this process, the polymer did not precipitate and the solution turned into a gel. The steel ball was then moved to the top of the gel by a magnet, and the gel was warmed at a rate of 6°C h⁻¹. The height *h* of the steel ball from a reference level was measured by a cathetometer at selected temperatures. On melting, the steel ball began to fall. Typical changes in *h* with temperature are shown in Figure 1. The temperature at which the horizontal and vertical straight lines intersected was defined as the gel-melting temperature. As in our previous study,⁶ the dependence of the gel-melting temperature on the weight of the steel ball was examined prior to a series of experiments, and the steel ball was chosen on this basis.

Measurement of Swelling Ratio

To analyze our experimental results by the theory proposed by Takahashi, Sakai and Kato,³ the interaction energy densities for the polymer-solvent pairs were estimated by measurement of the swelling ratio. 0.1 g of a branched low density polyethylene sample (density, 0.920 g cm⁻³ at 25°C and number-average molecular weight M_n , 1.76×10^4) was moulded into films which were then 60 Mrad irradiated by an electron beam so as to crosslink the polymer molecules. Soluble parts of the films were extracted by xylene at its boiling point for 24 h. The crosslinked films were dried and their weights were determined. The crosslinked films were swollen in *p*-xylene for 24 h at 72.7°C, the swelling ratio determined, and the volume fraction of polymer ϕ_2 in the swollen film calculated. The molecular weight M_c between crosslinking points was calculated from³

$$M_c = \frac{M_n d v_1 (\phi_2^{1/3} - 2\phi_2/v)}{2d v_1 (\phi_2^{1/3} - 2\phi_2/v) - M_n [\ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2^2]} \quad (1)$$

where d is the density of the film, v_1 , the molar volume of the solvent, M_n , the number-average molecular weight of the sample before cross-linking, v , the functionality of a crosslinked point, and χ_1 , the Flory-Huggins interaction parameter.

With $v=3$ and $\chi_1=0.511$ for the polyethylene + *p*-xylene system,⁷ M_c was determined to be 8.0×10^3 — 8.6×10^3 . Identical films were swollen in respective solvents at 40°C for 24 h and the swelling ratios determined. The χ_1 parameters for branched low density polyethylene in these solvents were calculated by eq 1 with this value of M_c .

RESULTS AND DISCUSSION

Solutions of branched low density polyethylene in decalin, tetralin, *o*-xylene, toluene and benzene were converted to thermo-reversible gels on cooling. The gel-melting temperature increased with polymer concentration. The relation between gel-melting temperature and polymer concentration in decalin is illustrated in Figure 2. Similar relations were obtained in other solvents. In dilute solutions,

no thermo-reversible gel was formed, but the polymer precipitated from the solution on cooling.

Eldridge and Ferry⁸ proposed the following empirical relation between gel-melting temperature T_m^g and volume fraction v_2 of poly-

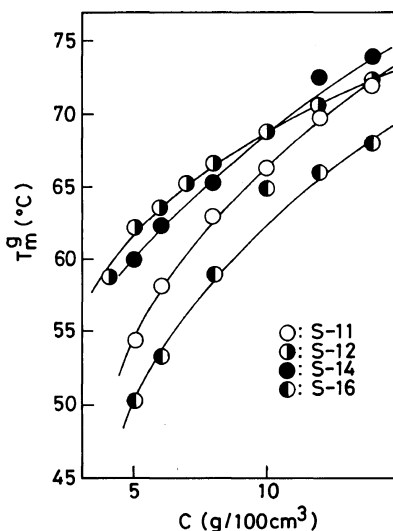


Figure 2. Relation between gel-melting temperature and concentration for branched low density polyethylenes in decalin.

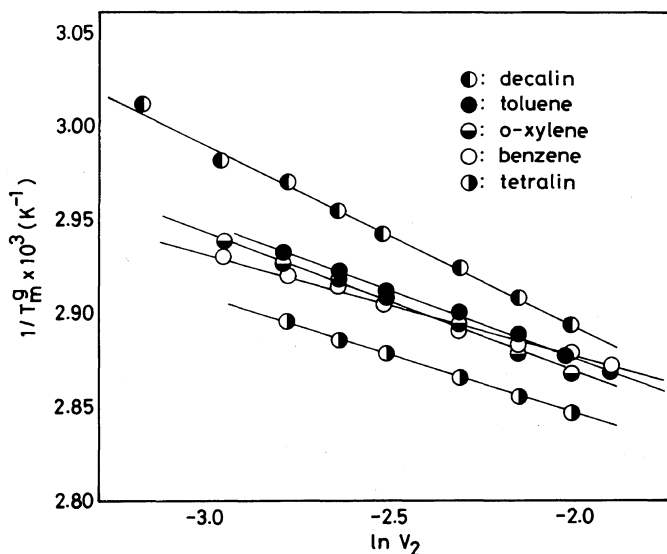


Figure 3. Relation between the reciprocal of gel-melting temperature and the logarithm of polymer concentration for S-12.

mer in the gel,

$$\ln v_2 = \text{const.} + \Delta H_m / T_m^g \quad (2)$$

where ΔH_m is the heat absorbed on formation of one mol of junction points. Eldridge and Ferry's plots for S-12 are illustrated in Figure 3 which indicates that Eldridge and Ferry's relation was obeyed for all solvent studied. Similar relations were obtained for other samples. However, the mechanism of gelation and dependence of the gel-melting temperature on molecular weight or branching degree could not be elucidated by this type of plot, being merely empirical.

Branched low density polyethylene has long chain branches and thus the theory of Takahashi, Sakai and Kato, which assumes a copolymeric character of branched polymers,³ is applicable to our data. According to this theory, the following equation can be derived assuming that branched polyethylene is an f -star branched polymer:

$$\frac{1}{T_m^g} = \frac{\zeta}{\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec}} \times \left(\frac{\Delta h_u}{T_m^0} + \frac{R V_A}{V_1} - R \ln X_A \right) - \frac{R}{\rho(\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec})} \times \{ \ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1] \} \quad (3)$$

where ζ and ρ are the ethylene-unit length and number of crystalline sequences in a crystallite, respectively, Δh_u , the heat of fusion of an ethylene unit, B' , the cohesive energy density defined by $\chi_1 = B' V_1 / RT$, σ_{ec} , the end interfacial free energy per crystalline sequence, T_m^0 , the melting temperature of linear polyethylene, X_A , the mole fraction of crystalline units, and V_A and V_1 , the molar volume of a crystalline unit and the solvent, respectively. When the values of parameters other than ρ and ζ in eq 3 are known, ρ and ζ can be estimated from gel-melting temperature data

Table II. Parameters values for branched low density polyethylene³

| | |
|---------------|--------------------------------------|
| σ_{ec} | 2840 cal mol ⁻¹ |
| Δh_u | 1920 cal mol ⁻¹ |
| T_m^0 | 418.6 K |
| V_A | 28 cm ³ mol ⁻¹ |

Table III. Estimated values of V_1 and B'

| Solvent | V_1 | B' |
|------------------|-----------------------------------|----------------------|
| | cm ³ mol ⁻¹ | cal cm ⁻³ |
| Decalin | 158.6 | 2.41 |
| Tetralin | 137.9 | 3.48 |
| <i>o</i> -Xylene | 123.0 | 3.60 |
| Toluene | 106.2 | 3.81 |
| Benzene | 91.0 | 4.91 |

Table IV. Molecular parameters values for branched low density polyethylenes

| Sample | $M_w \times 10^{-4}$ | λM_w | f | X_A |
|--------|----------------------|---------------|-----|-------|
| S-11 | 7.4 | 2.9 | 5 | 0.976 |
| S-12 | 16.1 | 6.8 | 9 | 0.974 |
| S-14 | 13.7 | 5.6 | 8 | 0.976 |
| S-16 | 17.5 | 8.9 | 11 | 0.970 |

as follows. Assuming an appropriate value for ρ , we plot $1/T_m^g$ against $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ and determine the intercept and slope of the plot. Then we can calculate ζ and ρ from the resulting values. This calculation is repeated until the assumed and calculated ρ values coincide. Among the parameters of eq 3, σ_{ec} , Δh_u , T_m^0 and V_A are characteristic of branched low density polyethylene, and hence the values proposed by Takahashi, Sakai and Kato³ (shown in Table II) were conveniently used. The molar volumes V_1 were calculated from the densities of the solvents, and the cohesive energy densities B' were determined by measuring the swelling ratios of the polymer in the respective solvents with results presented in Table III. The mole fraction V_A of crystalline units was calculated from

Sol-Gel Transition of Polyethylene Gel

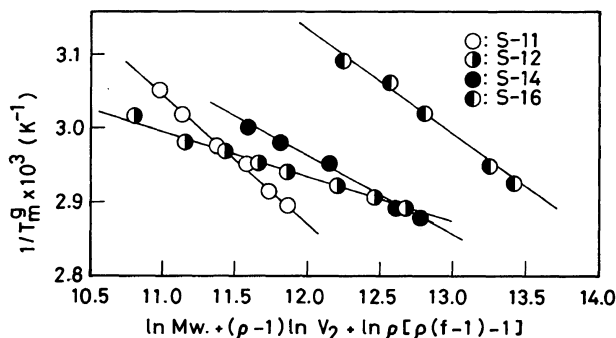


Figure 4. Relation between the reciprocal of gel-melting temperature and $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ in decalin.

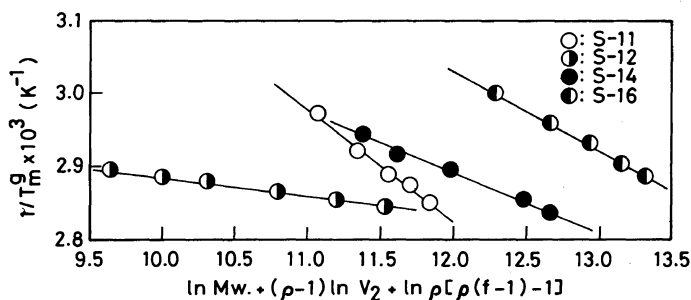


Figure 5. Relation between the reciprocal of gel-melting temperature and $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ in tetralin.

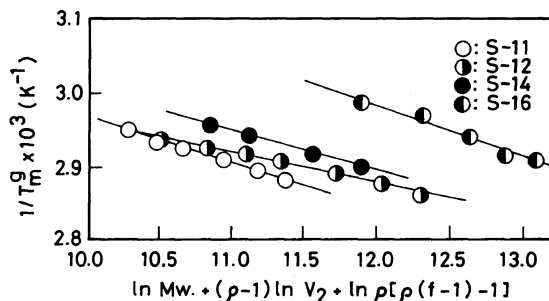


Figure 6. Relation between the reciprocal of gel-melting temperature and $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ in *o*-xylene.

$V_A = [1 - 0.001(\text{CH}_3/1000\text{C})]$, where $\text{CH}_3/1000\text{C}$ is the number of methyl groups per 1000 carbon atoms.³ f was taken to be $\lambda M_w + 2$, where λ is the branch density.³ The values of λ were calculated by the Zimm-Stockmayer method⁹ using the procedure presented in the previous paper.⁴ The molecular parameters so obtained for branched low

density polyethylenes are summarized in Table IV.

The results derived by applying the above method to our experimental data are shown in Figures 4–8, and the calculated values of ρ and ζ are summarized in Table V. It can be seen that the theory of Takahashi, Sakai and Kato is well applicable to the sol-gel transition

of branched low density polyethylene in a cyclohexane + carbon disulfide mixed solvent as well as in decalin, tetralin, *o*-xylene, toluene and benzene. It is likely that ρ and ζ are independent of the molecular weight, the number of branches per 1000 carbon atoms of the polymer and the solvent. In our previous paper,⁴ we showed that ρ and ζ were independent of the molecular weight of the polymer. The present results support the findings in previous study. However, the dependence of ρ and ζ on the branch degree could not be shown in the present study, since the branch degree of the sample did not vary systematically. Moreover, the values of ρ were too small to form crystalline nuclei in the gels. Our values of ρ and ζ should be compared with the values derived by other methods such as X-ray diffraction. This will be carried out at some future date.

In conclusion, the present study clarified the

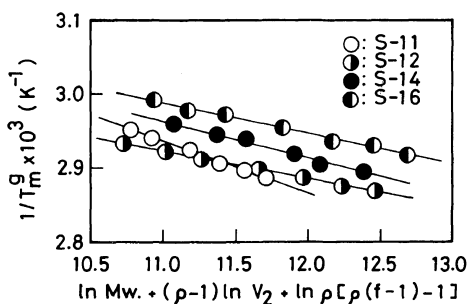


Figure 7. Relation between the reciprocal of gel-melting temperature and $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ in toluene.

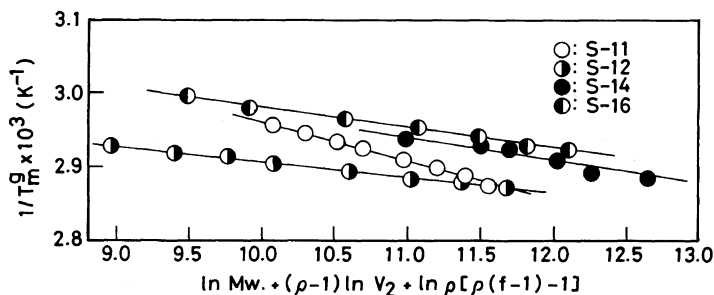


Figure 8. Relation between the reciprocal of gel-melting temperature and $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ in benzene.

following facts for the sol-gel transition of branched low density polyethylene in organic solvents. This polymer in decalin, tetralin, *o*-xylene, toluene and benzene is converted to a thermo-reversible gel on cooling. The gel-melting temperature depends on the polymer concentration and molecular weight, and its reciprocal varies linearly with the logarithm of

Table V. Estimated values of ρ and ζ

| Sample (LDPE) | Solvent | ρ | ζ |
|---------------|------------------|--------|---------|
| S-11 | <i>o</i> -Xylene | 2.4 | 9.6 |
| S-12 | | 2.9 | 11.3 |
| S-14 | | 2.6 | 9.7 |
| S-16 | | 2.5 | 8.2 |
| S-11 | Tetralin | 2.0 | 6.1 |
| S-12 | | 3.5 | 13.7 |
| S-14 | | 2.4 | 8.0 |
| S-16 | | 2.3 | 6.6 |
| S-11 | Decalin | 2.0 | 5.8 |
| S-12 | | 2.6 | 9.2 |
| S-14 | | 2.3 | 7.1 |
| S-16 | | 2.3 | 5.9 |
| S-11 | Toluene | 2.3 | 8.8 |
| S-12 | | 2.9 | 12.1 |
| S-14 | | 2.6 | 9.9 |
| S-16 | | 3.0 | 11.1 |
| S-11 | Benzene | 2.4 | 10.2 |
| S-12 | | 3.6 | 10.2 |
| S-14 | | 2.8 | 11.3 |
| S-16 | | 3.5 | 13.0 |

^a ρ , crystalline sequence of crystallites.

^b ζ , ethylene-unit length of crystallite.

the polymer concentration. The theory of Takahashi, Sakai and Kato is quite applicable to the systems studied, and allows calculation of the size of a crystalline junction in the gel. The sizes obtained in different solvents are nearly equal and independent of the molecular weight of the polymer.

Acknowledgement. The authors wish to express their sincere appreciation to Mr. Yoshihiro Motegi of the Ohita Laboratory, Showa Denko Co. for supplying the samples and making their characterization. Thanks are also due to Dr. Toshio Shigematsu of Ibaragi Electrocommunication Laboratory, Nippon Telegraph and Telephone Corporation for irradiating the polymers with an electron beam. One of us (H. Matsuda) is grateful to Showa Denko Co. for a grant by which this work was possible. Partial support was also obtained

through a Grant-in-Aid from the Ministry of Education.

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