Melting Temperature of Thermally Reversible Gel.
VI. Effect of Branching on the Sol–Gel
Transition of Polyethylene Gels

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ABSTRACT: The gel-melting temperatures of branched polyethylene–cyclohexane–carbon disulfide gels were measured. Branched polyethylenes having a different number of long-branching points were used. The reciprocal of the gel-melting temperature is a linear function of the logarithm of the polymer concentration. A theory which predicts the gel-melting temperature of branched crystalline copolymers is given. Analysis of the experimental data suggests that the size of the crystalline junction decreases with an increase in the number of long-branching points.
    KEY WORDS   Sol–Gel Transition / Branched Polyethylene / Gel / Gel-Melting Temperature / Polyethylene /

It is well known that polyethylene is precipitated as crystalline lamella from its dilute solution upon cooling. However, another type of crystallization is known, in which the separation of the crystalline phase from solution does not occur, but the whole solution converts to a gel, indicating crystallinity.[1−11]

It is well recognized that the copolymeric character of a crystalline polymer is conductive to gelation.[1,11] Polyethylene, which has both short and long branches, is a crystalline copolymer and, indeed, Matsuda, Araki, and Kuroiwa[12] discovered that on cooling a branched polyethylene–cyclohexane–carbon disulfide solution, the whole system is converted to a gel instead of separating into crystalline phases. Moreover, they found that the gel is crystalline, since X-ray diffraction pattern indicated the crystalline order of the polyethylene crystal. If gelation takes place, cross-linking loci should be present in the system. It is considered that the crystallites perform the role of cross-linking loci. They reported gel-melting temperatures as a function of polymer concentration as well as molecular weight; however, no detailed thermodynamic analysis of a gel–sol transition was attempted. In the previous papers of this series, we presented a thermodynamic analysis of the gel-melting temperature of various gels formed by synthetic polymers. In this

paper, we extend the previous theoretical treatment of the gel-melting temperature to include branched polymers and the new theory is compared with experimental gel-melting temperature data measured for well characterized polyethylenes having long branches.

EXPERIMENTAL

Materials

Three polyethylene samples each having a different number of long branches have been used. Characterization of these samples was carried out by Nakano and Goto.[13] And their characteristics are given in Table I. Benzene, cyclohexane, and carbon disulfide were distilled before use. Benzophenone (Nakarai Chem. Ltd.) was used as received.
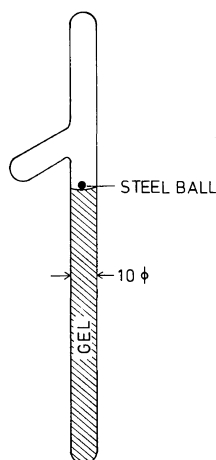
Gel-Melting Temperature

The gel-melting temperature apparatus shown in Figure 1 was used. The apparatus has an arm in which a steel ball (less than 100 mg wt) is placed. A weighted amount of polyethylene was placed in the bottom of the apparatus and a weighted amount of 1 : 1 volume ratio cyclohexane and carbon disulfide mixed solvent was added. The apparatus was then sealed. It was placed in a thermostat which maintained at 80°C and the polymer sample was dis-

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Table I. Characteristics of branched polyethylene

Samples	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	CH$_3$/1000C[a]	$\lambda \times 10^{5b}$	λM_w
A	2.30	12.6	27	5.7	7.18
B	2.56	10.1	22	0	0
C	2.24	15.1	23	2.7	4.07

[a] Fraction of short branches.
[b] $\lambda M_w = m$ is the number of branch points of long branches per polymer.

Figure 1. The gel-melting temperature apparatus.

solved. After dissolution, the apparatus was placed in a thermostat kept at 20°C, and gelation was carried out for 16 h. After gelation, the steel ball was placed on the top of gel by magnetic manipulation. The gel was then heated at the rate of 0.4°C min^{-1} and the height of the steel ball was recorded with temperature. When the gel melts, *i.e.*, converts to a sol, the steel ball starts to move downward. Typical examples of measurements are shown in Figure 2. The intersection of two straight lines was taken as the gel-melting temperature. The effect of the weight of the steel ball on gel-melting temperatures was examined. It was found that the gel-melting temperature did not depend very much on the weight of the ball as long as it was less than 100 mg.

Swelling Experiment

A low-density polyethylene film (0.5 mm thickness) [$M_n = 2.37 \times 10^4$] was immersed in a 5 wt/wt% benzene solution of benzophenone for 24 h. Then the film was irradiated by UV light for 200 min and
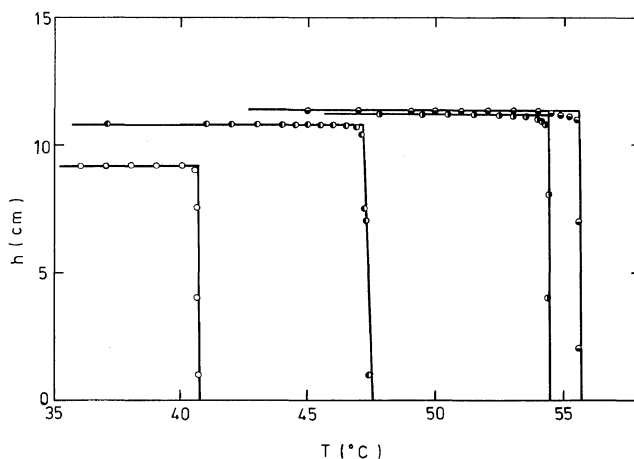
Figure 2. Examples of the measurements of gel–sol transition temperatures. Sample A. Volume fraction of polymers: ○, 0.065; ◐, 0.079; ◑, 0.097; ◒, 0.113.

photocross-linked. The film was extracted by boiling benzene in a Soxhlet apparatus.

Swelling experiment was carried out as follows: after the weight of the film was determined, the cross-linked film was swelled in p-xylene for 24 h at 72.7°C and the weight of swelled film was determined.

From the swelling ratio, the volume fraction of polymer v_2 was determined. The molecular weight between the cross-linked points M_c was calculated by[14]

$$M_c = M_n d v_0 (v_2^{1/3} - 2v_2/v)/\{2 d v_0 (v_2^{1/3} - 2v_2/v)$$
$$- M_n [\ln(1 - v_2) + v_2 + \chi_1 v_2^2]\} \qquad (1)$$

where d is the density of the film, v_0 is the molar volume of solvent, v is the functionality of a cross-linked point, M_n is the number-average molecular weight of the sample before cross-linking and χ_1 is the interaction parameter. Making use of $v = 3$ and $\chi_1 = 0.511$ for polyethylene–p-xylene pair,[15] M_c was determined as 6138.

Having established M_c, the same film was swelled in a 1:1 volume mixture of cyclohexane and carbon disulfide at 25°C, and the swelling ratio was determined. The χ_1 parameter for polyethylene–cyclohexane-carbon disulfide mixed solvent was calculated by eq 1.

RESULTS AND DISCUSSION

When polethylene–cyclohexane–carbon disulfide solutions were converted to gels, they exhibited turbidity. The gel converted to a sol at about 40 to 70°C depending on the number of long branches. The increase in the number of long branches resulted in a lower gel-melting temperature ($T_m{}^g$). Gel-melting temperatures increased with increase in polymer concentration. In Figure 3, $1/T_m{}^g$ is plotted against the logarithm of polymer concentration and straight lines are obtained, indicating that the relationship due to Eldridge and Ferry[16] holds; that is,

$$\ln v_2 = \mathrm{const} + \Delta H_m / R T_m{}^g \qquad (2)$$

Here, ΔH_m is the heat absorbed on formation of a mole of the junction points. From Figure 3, it is apparent that ΔH_m depends on the number of long branches in each polyethylene sample. However, the Eldridge and Ferry relationship does not indicate the molecular mechanism or model of gelation. According to Matsuda, Araki, and Kuroiwa,[12] the
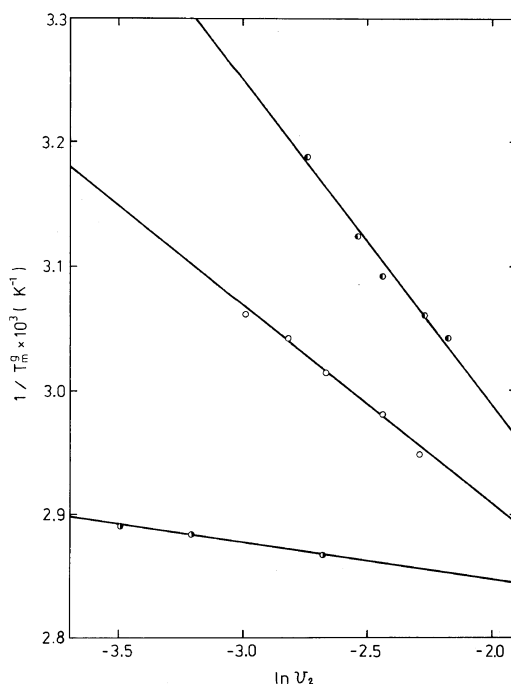

Figure 3. The reciprocals of the gel-melting temperature $vs.$ $\ln v_2$ plots for samples: ◖, A; ◑, B; ○, C.

polyethylene–cyclohexane–carbon disulfide gel exhibits wide angle X-ray diffraction. Therefore, crystallites consisting of ethylene unit behave as cross-linking junction points.

Branching points in a branched polyethyene are trifunctional and these points exist along a trunk chain. However, to simplify the theoretical treatment of a gel-melting temperature of a branched polymer, an unorthodox way is to assume that the branched polyethylene is an f-star branched polymer. Then, if a crystallite is ζ ethylene-unit long and consists of ρ crystalline sequences, the theory in the Appendix assumes that only one equilibrium is involved, $i.e.$,

$$\rho \text{ (crystalline sequences)} \rightleftharpoons 1 \text{ crystallite} \qquad (3)$$
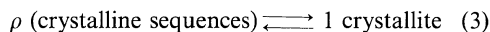
Though the gel-melting point is not the thermodynamic singularity, according to this theory, the gel-melting temperature is given as follows.

$$1/T_m{}^g = \zeta/(\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec})$$
$$\times (\Delta h_u / T_m{}^\circ + R V_A / V_1 - R \ln \chi_A)$$
$$- R/\rho(\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec})$$
$$\times \{\ln \langle M_w \rangle + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]\} \qquad (4)$$

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In the equation, Δh_u is the heat of fusion of an ethylene unit, B' is the cohesive energy density defined by $\chi_1 = B'V_1/RT$, σ_{ec} is the end interfacial free energy per crystalline sequence, T_m° is the melting temperature of polyethylene, X_A is the mole fraction of crystalline units, M_w is the weight-average molecular weight, v_2 is the volume fraction of the polymer in the gel, and V_A and V_1 are the molar volumes of a crystalline unit and solvent, respectively.

For a linear polymer, f is equal to 2 and for the branched polyethylene with the number $m(=\lambda M_w)$ of branching points in the long branches, f is $(m+2)$. Equation 4 differs from our previous equation for the gel-melting temperature,[1,17] in which the functionality ρ of crystalline junction was neglected.

If quantities other than ρ and ζ are known, then eq 4 enable us to estimate both ρ and ζ from experimental gel-melting temperatures. The procedure is as follows. Assuming a value for ρ, then $1/T_m^g$ is plotted against

$$\{\ln \langle M_w \rangle + (\rho - 1)\ln v_2 + \ln \rho[\rho(f-1)-1]\}$$

and from the intercept and the slope thus obtained, ζ and ρ are evaluated. This procedure is repeated until the assumed ρ and the evaluated ρ coincide. From the swelling experiment in the cyclohexane–carbon disulfide mixed solvent, χ_1 was estimated to be 0.636 resulting $B' = 4.45$ cal ml^{-1}. For σ_{ec}, the value 2840 cal mol^{-1} of sequence estimated for ethylene–vinyl acetate copolymer gel[2] was employed. X_A is identical with $[1 - 0.001(CH_3/1000C)]$ and f is taken to be equal to $\lambda \langle M_w \rangle + 2$. Making use of $\Delta h_u = 1920$ cal mol^{-1}, $T_m^\circ = 418.6$ K $V_A = 28$ ml mol^{-1} and $V_1 = 84.67$ ml mol^{-1}, the above procedure was applied for estimating both ρ and ζ. The results are summarized in Table II and shown in Figures 4 and 5.

Table II. The estimated ρ and ξ

Samples	ρ	ξ
A	2	4.7
B	14	33
C	2	5.8

The melting temeperature of normal paraffin having a carbon number of 66 is 376.8 K and the gel-melting temperature of sample B ($\zeta = 33$ ethylene units) is 346 K. If the melting point depression of crystallites caused by the solvent is taken into consideration, then the values ρ and ζ for sample B are reasonable. However, for samples A and C, the estimated values of ζ are too small, since the melting temperature of normal paraffin of carbon number 11[18] is 245 K, which is lower than the gel-melting
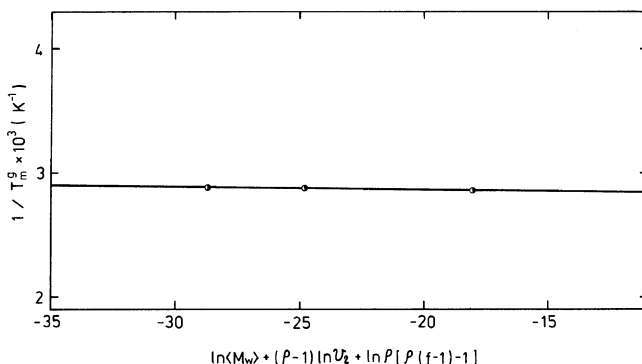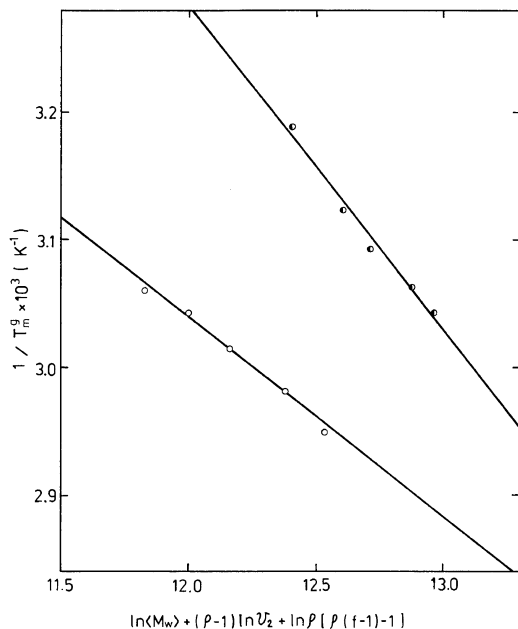

Figure 4. The reciprocals of the gel-melting temperarure vs.
$$\{\ln \langle M_w \rangle + (\rho - 1)\ln v_2 + \ln \rho[\rho(f-1)-1]\}. \quad \text{Sample B.}$$

Figure 5. The reciprocals of the gel-melting temperature vs.

$$\{\ln \langle M_w \rangle + (\rho - 1) \ln v_2 + \ln \rho[\rho(f-1)-1]\}$$

for samples: ◑, A; ○, C.

points, i.e., $T_m{}^g \simeq 320 \text{ K}$ for sample A and $T_m{}^g \simeq 330 \text{ K}$ for sample C. The estimated ζ depends crucially on the assumed σ_{ec}, and we selected $\sigma_{ec} = 2840 \text{ cal/(mol of sequence)}$. And this value is also identical to the interfacial free energy of polyethylene single crystals. It was seen that a much higher σ_{ec} value results in a higher ζ. Because of the uncertainty in the value of σ_{ec} for fringed micellar crystallites, we, therefore, do not give much credence to an absolute value of ζ; however, the order of crystallite size is correct since the gel-melting points are also in this order. The turbidity of gels is also in this order, since crystallite size and number determine the turbidity. The value of ρ does not depend so much on an assumed value of σ_{ec}. The value, $\rho = 2$ is the minimum number of crystalline sequences to form crystalline nuclei, which appear at the gel-melting point.

Since branched polyethylene is not a star branched polymer, the assumption of crystallization of star branched polymers given in the Appendix is open to criticism. If trunk chains are incorporated into the crystallite, then the value of f is varied. However, it was found that the variation in the value of f did not affect very much the values of ρ and ζ estimated.

Thus, we may expect that the assumption of a star polymer is not entirely wrong or that branched polyethylene is resembles a star polymer.

In conclusion, the crystallite size decreases with an increase in the number of long branches resulting from a lower gel melting point.

APPENDIX

Consider an f star branched crystalline copolymer in a solution, and that these ρ copolymers gather to form a crystallite consisting of ρ crystalline sequences and ζ units long as in Figure A-1. The branches of the crystallized copolymers further crystallize to form other crystallites having ρ sequences. These crystallites act as cross-linking junctions, and so the critical branching coefficient, α_c, is given by[19]

$$\alpha_c = 1/[\rho(f-1)-1] \qquad \text{(A-1)}$$

Denoting the critical number of crystallites as N (g ml^{-1}), α_c may be alternatively written as

$$\alpha_c = N/(v_2/xV_1\rho) \qquad \text{(A-2)}$$

where v_2 is the volume fraction of the polymer, x is the number of segments in a polymer, V_1 is the molar volume of the solvent. The following equilibrium is considered to be
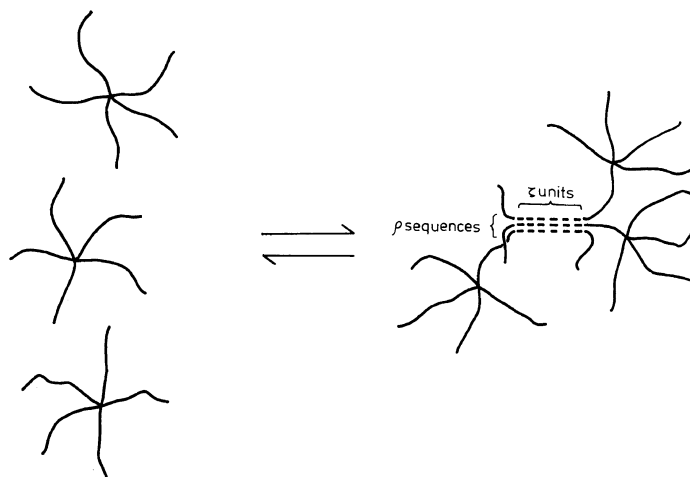
$$\rho \text{ potential crystalline sequences} \rightleftharpoons$$
$$1 \ \rho\text{-fold crystalline junction} \qquad \text{(A-3)}$$
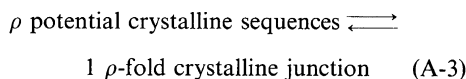
The equilibrium constant may thus be written as

$$K = N\bar{v}/v_2{}^\rho = \exp(-\Delta F/RT) \qquad \text{(A-4)}$$

where $\bar{v}$ is the partial specific volume of a crystallite and ΔF is the free-energy change accompanying the transformation of $\rho\zeta$ units from solution to a crystallite[1]:

$$\Delta F = \rho[2\sigma_{ec} - \zeta\Delta f_u + \zeta RT(V_A/v_1)(1-\chi_1)$$
$$- \zeta RT \ln X_A] + 2\zeta\sigma_u(\pi\rho)^{1/2} \qquad \text{(A-5)}$$

$$\simeq \rho[2\sigma_{ec} - \zeta\Delta f_u + \zeta RT(V_A/v_1)(1-\chi_1)$$
$$- \zeta RT \ln X_A] \qquad \text{(A-6)}$$

Figure A-1. ρ of f-star branched crystalline copolymers gather to form a crystallite with ρ crystalline sequences and ξ units long.

In the above equation, σ_{ec} and σ_u are the end and the lateral interfacial free energies, Δf_u is the free energy of fusion per crystalline unit, χ_1 is the interaction parameter, X_A is the mole fraction of crystalline units, and V_A and V_1 are the molar volumes of a crystalline unit and solvent, respectively. In eq A-6, the contribution of the lateral interfacial free-energy term is neglected since in general, σ_u is very small. From eq A-1, A-2, A-4, and A-6, we obtain,

$$v_2 \bar{v}/\{x' v_2{}^\rho \rho[\rho(f-1)-1]\}$$

$$= \exp\{-\rho[2\sigma_{ec} - \zeta\Delta f_u + \zeta RT(V_A/V_1)(1-\chi_1)$$

$$-\zeta RT \ln X_A]\}/RT \qquad (A-7)$$

where $x' = xV_1$. Taking the logarithm of eq A-7 and making use of $x'/\bar{v} = M$, $\chi_1 = B'V_1/RT_m{}^g$ and $\Delta f_u = \Delta h_u(T_m{}^\circ - T_m{}^g)/T_m{}^\circ$, where $T_m{}^\circ$ is the melting temperature of a perfect crystal and Δh_u is the heat of fusion per monomer unit, we obtain

$$1/T_m{}^g = \zeta/(\zeta\Delta h_u + \zeta B'V_A - 2\sigma_{ec})$$

$$\times (\Delta h_u/T_m{}^\circ + RV_A/V_1 - R \ln X_A)$$

$$- R/\rho(\zeta\Delta h_u + \zeta B'V_A - 2\sigma_{ec})$$

$$\times \{(\ln\langle M_w\rangle + (\rho-1)\ln v_2 + \ln \rho[\rho(f-1)-1]\} \qquad (A-8)$$

Here we used the weight-average molecular weight.

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