Sol-Gel Transition of Fractionated Low Density Polyethylene in Cyclohexane-Carbondisulfide Mixed Solvent

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ABSTRACT: Sol-gel transitions of a series of fractionated low-density polyethylenes in cyclohexane-carbondisulfide were studied. Gelation temperatures increased with polymer concentration as well as molecular weight. Experimental data were analyzed by a theory proposed by Takahashi, Sakai and Kato for the gel-melting temperature of branched polymers. This theory was found to apply well to the experimental data. The results of our study suggest that the size of the crystalline junction is independent of the molecular weight of fractionated samples.

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

It is well known that polyethylene withstands chemical reagents and is soluble in organic solvents only at elevated temperatures. This is a very good property of polyethylene but one which makes it difficult to measure molecular weight and solution properties. A few years ago, Nita Das and Palit reported that low density polyethylene was soluble near room temperature in binary mixtures of organic solvents such as xylene-carbondisulfide, cyclohexane-carbondisulfide, cyclohexane-trichloroethylene and cyclohexane-cyclohexanone systems.¹ Their experiments were followed over a wide range of concentrations in our laboratory; we found that solutions of low density polyethylene in cyclohexane-carbondisulfide were converted to gels on cooling and the gels reverted to solutions when were warmed near room temperature.^{2,3} Moreover, we found from X-ray diffraction patterns that the gels were crystalline. Our experimental results showed that gel-formation temperature depended on the molecular weight of the polymer as well as the concentration of the solution. Recently, Takahashi, Sakai, and Kato carried out similar experiments using three unfractionated branched polyethylenes and proposed a new theory for treating the gel-melting temperature of a branched polymer.⁴ Their

treatment is useful for estimating the size of a crystalline junction in the gel. In this study, gelation temperatures were measured for a series of fractionated low density polyethylene in cyclohexane-carbondisulfide and compared with the theory of Takahashi, Sakai, and Kato.

EXPERIMENTAL

Materials

Six fractions of low-density polyethylene (branched polyethylenes) fractionated from a sample were used. Fractionation and characterization of the samples were carried out by Motegi of the Ohita Laboratory, Showa Denko Co. The physical properties of the samples are shown in Table I. Although the molecular weights of the samples are different, the numbers of methyl groups per 1000 carbon atoms are nearly equal. Cyclohexane and carbondisulfide were distilled before each measurement. The solvent system used in this experiment was a mixture of cyclohexane and carbondisulfide (in volume 1:1).

Gelation Temperature

Measurement of gelation temperature was carried

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

Fraction	$[\eta]$, (100 cm ³ /g) tetralin at 130°C	$M_w \times 10^{-4}$	CH ₃ /1000C
Fr-4	0.48	3.0	32.0
Fr-5	0.71	6.5	32.5
Fr-6	1.08	22.2	32.3
Fr-7	1.54	87.0	31.8
Fr-9	1.88	330	32.9
Fr-10	1.75	200	31.3

^a M_w were measured by GPC. CH₃/1000C is the number of methyl groups per 1000 carbon atoms determined by infrared analysis.

out as follows. A definite weight of the polymer and volume of the mixed solvent were placed in a glass tube and sealed. The polymer was dissolved completely at 80°C and the glass tube was immersed in a thermostat maintained at a constant temperature. After 24 hours, the solution in the glass tube was examined to see whether a gel was formed. To make sure that the solution converted to a gel, the glass tube was turned upside down. When the content did not flow, we decided that solution had been converted to a gel. By varying the temperature of the thermostat, the highest temperature of the gel formation was established as the gelation temperature. Although this temperature was slightly different from the gel-melting temperature measured by Takahashi, Sakai and Kato, we assumed that the gelation temperature was identical with the gel-melting temperature. The results were analyzed on the basis of the theory of Takahashi, Sakai, and Kato.

RESULTS AND DISCUSSION

Solutions of low density polyethylene in cyclohexane-carbondisulfide were converted to gels on cooling. The gels were thermoreversible. The gelation temperature increased with polymer concentration, and the reciprocal of the gelation temperature varied linearly with the logarithm of polymer concentration. Examples of the results are shown in Figure 1. Eldridge and Ferry suggested the relation,⁵

$$\ln v_2 = \text{const} + \Delta H_m / RT_m \quad (1)$$

where ΔH_m is the heat absorbed on formation of one mole of junction points and v_2 is the volume

Figure 1. Relationship between the reciprocal of gelation temperature and the logarithm of polymer concentration.

fraction of polymer in the solution. The behavior in Figure 1 is identical to that observed in sol-gel transitions of many polymer-solvent systems. Moreover, gelation temperatures increased with molecular weight at the same polymer concentration in the lower molecular weight region and converted to a definite temperature in the higher molecular weight region.

Low density polyethylene has long chain branches, so that the theory of Takahashi, Sakai, and Kato is applicable to our data. According to this theory, the following equation was obtained, assuming that branched polyethylene is a f -star branched polymer.⁴

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

where T_m^g is the gel melting temperature which is assumed to be equal to the gelation temperature in this study, ζ is the ethylene-unit length in a crystallite, ρ is the crystalline sequence in a crystallite, 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^0 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 the solvent, respectively. When the values of quantities other than ρ and ζ are known, the values of ρ and ζ can be estimated from the gel-melting temperature data as follows. Assuming an appropriate value of ρ , we plot $1/T_m^g$ against

$$\ln M_w + (\rho - 1) \ln v_2 + \ln \rho [f - 1] - 1$$

and determine the intercept and slope of the plot. We then calculated ζ and ρ from the intercept and slope values. We repeat this operation until the assumed ρ coincides with the calculated one. Since our polymer-solvent system was identical with that of Takahashi, Sakai, and Kato, the values proposed in their paper⁴ were used for the parameters of eq 2, and are shown in Table II.

Table II. Values of parameters of eq 2 for low density polyethylene in cyclohexane-carbondisulfide⁴

Parameters	Values
B'	4.45 cal mol ⁻¹ .
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 .
V_1	84.67 cm ³ mol ⁻¹ .

The mol fraction X_A of crystalline units is given by $[1 - 0.001(\text{CH}_3/1000\text{C})]$, where $\text{CH}_3/1000\text{C}$ is the number of methyl groups per 1000 carbon atoms. f is taken to be equal to $[\lambda M_w + 2]$, where λ is the branch density. According to Zimm and Stockmayer, λ is determined from the intrinsic viscosities of branched and linear polymers by⁶

$$g_\eta = [\eta]_{\text{branch}} / [\eta]_{\text{linear}} \quad (3)$$

$$g_\eta = \frac{6}{m} \left[\frac{1}{2} \left(\frac{2+m}{m} \right)^{1/2} \ln \left\{ \frac{(2+m)^{1/2} + m^{1/2}}{(2+m)^{1/2} - m^{1/2}} \right\} - 1 \right], \quad (4)$$

$$m = \lambda M_w \quad (5)$$

The intrinsic viscosities of linear polymers in tetralin at 130°C were calculated from the following equation,⁷

$$[\eta] = 5.60 \times 10^{-4} M_w^{0.694} \quad (6)$$

The molecular parameters so obtained for fractionated low density polyethylene are shown in Table III.

Table III. Values of molecular parameters of fractionated low density polyethylenes

Fraction	$M_w \times 10^{-4}$	λM_w	f	X_A^a
Fr-4	3.0	3.1	5	0.968
Fr-5	6.5	4.7	7	0.968
Fr-6	22.2	12.2	14	0.968
Fr-7	87.0	34.8	37	0.968
Fr-9	330	101.1	103	0.967
Fr-10	200	69.6	72	0.969

^a The average value $X_A = 0.968$ was used for calculation.

Figure 2. Reciprocal of gelation temperature vs. $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho [f - 1] - 1$ for Fr. 4, 5, and 6.

The results of the application of the above method to our experimental data are shown in Figures 2, 3, and 4, and the values of ρ and ζ are summarized in Table IV. The theory of Takahashi, Sakai, and Kato is well applicable to sol-gel transition of branched polyethylene in the cyclohexane-

Figure 3. Reciprocal of gelation temperature vs. $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ for Fr. 7.

Figure 4. Reciprocal of gelation temperature vs. $\ln M_w + (\rho - 1) \ln v_2 + \ln \rho[\rho(f - 1) - 1]$ for Fr. 9 and 10.

Table IV. Values of ρ and ζ

Fraction	ρ	ζ
Fr-4	2	6.2
Fr-5	3	9.2
Fr-6	4	11.3
Fr-7	3	8.4
Fr-9	4	8.7
Fr-10	4	8.9

carbendisulfide system and the reasonable values of ρ and ζ are obtained. In Fr. 4, the value of ρ is 2, which is the minimum number of crystalline se-

quences to form crystalline nuclei. Therefore, this value may not be very accurate, since our method of measuring gelation temperature is less reliable for low molecular weight samples. Except for Fr. 4, the crystalline junction sizes are nearly equal to each other and independent of the molecular weight of the sample. However, the crystalline junction sizes should be compared with those obtained by other methods such as X-ray diffraction. This problem is left for future study.

In conclusion, the following results were obtained for the sol-gel transition of a series of fractionated low density polyethylenes in the cyclohexane-carbendisulfide system. The gelation temperature increases with concentration as well as with molecular weight of the polymer and the reciprocal of the gelation temperature has a linear relationship to the logarithm of polymer concentration. The theory of Takahashi, Sakai, and Kato is applicable well to this system and the size of a crystalline junction in the gel can be obtained by this theory. The sizes obtained ($\rho \div 3 \sim 4$, $\zeta \div 9$) are a nearly equal to each other and are independent of the molecular weight of a polymer in a series of fractionated samples.

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REFERENCES

1. Nita Das and S. R. Palit, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1025 (1973).
2. H. Matsuda, K. Araki, M. Yamada, and S. Kuroiwa, *Rep. Prog. Polym. Phys. Jpn.*, **20**, 69 (1977).
3. H. Matsuda and S. Kuroiwa, *Rep. Prog. Polym. Phys. Jpn.*, **22**, 45 (1979).
4. A. Takahashi, M. Sakai, and T. Kato, *Polym. J.*, **12**, 335 (1980).
5. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).
6. B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **12**, 1301 (1949).
7. T. Hama, K. Yamaguchi, and T. Suzuki, *Makromol. Chem.*, **155**, 283 (1972).