SHORT COMMUNICATION

Sol-Gel Transition of Low-Density Polyethylene in Decalin, Tetralin and *o*-Xylene

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In previous papers,^{1,2} we reported the phenomenon that solutions of low-density polyethylene in cyclohexane-carbon disulfide were converted to gels with cooling and the gels were converted to solution near room temperature with warming. Recently, Takahashi, Sakai, and Kato³ proposed a new theory for treating the sol-gel transition of a branched polymer-solvent system and estimated the size of crystalline junctions in the gel of unfractionated low-density polyethylene in cyclohexane-carbon disulfide. We also studied sol-gel transitions of a series of fractionated low-density polyethylenes in cyclohexane-carbon disulfide and reported that the size of crystalline junction did not depend upon the molecular weight of the samples.⁴ However, this theory concerned a branched polymer and a pure solvent system.³ Hence, in order to analyze the data of the sol-gel transition of polyethylene accurately, it is desirable to carry out experiments with pure solvents. Moreover, it is of interest to see whether the sol-gel transition takes place only in cyclohexane-carbon disulfide, and whether the sol-gel transition is one of the general properties of low-density polyethylene. Therefore, we looked for a solvent in which low-density polyethylene dissolves and the solution forms a thermoreversible gel. We found that low-density polyethylenes in ordinary organic solvents, such as decalin, tetralin, *o*-xylene and toluene, form thermoreversible gels and sol-gel transition may be one of the general properties of low-density polyethylene. However, it takes a long time to analyze the experiments of all the systems. Thus, in this paper, only the sol-gel transition of low-density polyethylene in decalin,

tetralin and *o*-xylene is reported.

EXPERIMENTAL

Materials

Three unfractionated low-density polyethylene samples were used. Each sample had a different number of long chain branching and molecular weight. The samples were supplied and characterized by Motegi of Ohita Laboratory, Showa Denko Co.⁵ The physical properties of the samples are shown in Table I. The samples were dissolved in xylene at the boiling point and precipitated in cooled methanol. They were then dried under reduced pressure. Decalin, tetralin, and *o*-xylene were purified by the ordinary method before use.

Gel-Melting Temperature

Solutions of low-density polyethylene in decalin, tetralin and *o*-xylene, with concentrations higher than about 3 wt%, were converted to gels with cooling and the gels were converted to solutions with warming. Usual phase separation took place in the range of dilute solutions.

The gel melting temperatures were measured by the method proposed by Takahashi, Sakai, and Kato.³ The apparatus is shown in Figure 1. A small steel ball (about 30 mg wt) is placed in an arm of the apparatus.

A specified weight of low-density polyethylene and volume of the solvent were placed in the apparatus and sealed. The polymer was dissolved completely at 150°C and the apparatus was immersed for 40 h in a thermostat regulated at con-

Table 1. Physical properties of low-density polyethylene samples^a

Sample	Density	$[\eta]$ (100 cm ³ g ⁻¹) Tetralin at 130°C	$M_w \times 10^{-4}$	CH ₃ /1000 C
	g cm ⁻³			
S-11	0.921	0.87	7.4	24.2
S-14	0.923	1.10	13.7	24.2
S-16	0.917	1.07	17.5	30.4

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

Figure 1. The apparatus of gel-melting temperature measurement. **Figure 2.** Examples of the measurements of gel-melting temperatures. Sample, S-16; $M_w = 17.5 \times 10^4$. Solvent, *o*-xylene. Concentration: —○—, 5 wt%; —●—, 8 wt%; —◐—, 14 wt%.

stant temperature. The gels were formed at 10°C for decalin and tetralin solutions, and at 30°C for *o*-xylene solutions. After 40 h, the solutions were converted to gels which exhibited turbidity. Then, the steel ball was placed on top of gel by a magnet and the gel was warmed at a rate of 6°C/h. The position of the steel ball from the reference level was measured by a cathetometer at different temperatures. When the gel melted, the steel ball began to fall. Typical examples of the results are shown in

Figure 2. According to Takahashi, Sakai, and Kato,³ the temperature at which two straight lines intersect is taken as the gel-melting temperature. The dependence of the gel-melting temperature on the weight of the steel ball was examined before the experiments and the steel balls, which give the gel-melting temperature independent of their weight, were selected.

RESULTS AND DISCUSSION

The solutions of low density polyethylene in decalin, tetralin, and *o*-xylene, with concentrations higher than about 3 wt%, were converted to gels with cooling and the gels were thermoreversible. In the range of dilute solution, the usual phase separation took place on cooling. Since all gels exhibited turbidity, it seems that the gels were cross-linked by many small crystalline junctions as in the case with low density polyethylene gels formed in a cyclohexane-carbon disulfide mixed solvent. Therefore, it is desirable to examine the X-ray diffraction patterns of the gels.

The relationships between the reciprocal gel-melting temperature and the logarithm of polymer concentration are shown in Figures 3, 4, and 5. In all these systems, the relationship of Eldridge and Ferry⁶ is satisfied:

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

where ΔH_m is the heat absorbed on formation of one mole of the junction point, v_2 is the volume fraction of the polymer in the gel and T_m^g is the gel-melting temperature. This behavior is identical with that observed for many crystalline polymer gels. The dependence of gel-melting point on molecular weight and number of long chain branching is not yet clear, because our data are insufficient.

Figure 3. The relations between the reciprocals of gel-melting temperatures and $\ln v_2$ in decalin.

Figure 4. The relations between the reciprocals of gel-melting temperatures and $\ln v_2$ in tetralin.

Figure 5. The relations between the reciprocals of gel-melting temperatures and $\ln v_2$ in *o*-xylene.

Systematic measurements of sol-gel transition in toluene are also being carried out at our laboratory. The dependence of the size of crystalline junction in the gel on the solvent must be investigated, but application of the theory requires knowledge of the values of cohesive energy density which can be measured by the swelling experiment.³ Detailed results will be reported in the future. Our experiments suggest that the sol-gel transition in organic solvents is one of the general properties of low-density polyethylene and that a sol-gel transition may take place in a solution of polypropylene in organic solvents. Indeed, preliminary investigations show that the solutions of polypropylene in decalin and tetralin are transformed to gels on cooling and that the gels are converted to solutions when heated.

According to Takahashi, Nakamura, and Kagawa, the copolymeric character of a crystalline polymer is conducive to gelation.⁷ Low-density polyethylene has both short and long branches in the molecule and is a crystalline copolymer. Polypropylene is also a stereo-regular copolymer. In consideration of this, sol-gel transitions of low-density polyethylene and polypropylene in organic solvents seem to be general properties of copolymers. It is of interest to note whether sol-gel transition takes place in the case of linear polyethylene in organic solvents.

Since polyethylene and polypropylene are widely used materials, our experiments may lead to some industrial applications of these polymers.

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