

Thermoreversible Gelation Mechanism of Polystyrene/CS₂ Solutions

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ABSTRACT: The gelation of P α MS/CS₂ solution was investigated to compare with atactic-(at-) and isotactic-(iso-)polystyrene (PS)/CS₂ systems. Gel melting temperature of poly(α -methyl)styrene (P α MS)/CS₂ was much higher than that of at-PS/CS₂ gels at the same polymer concentration and molecular weight. This implies that the chemical structure of the chains, in particular the side group of the chain, has significant influence on the gelation. The mixtures of at-PS/P α MS/CS₂ and at-PS/iso-PS/CS₂ also can form thermo-reversible gels on cooling. The melting temperature of at-PS/P α MS/CS₂ gels shifts to higher temperature with increasing weight fraction of P α MS. In contrast, no obvious change was observed in the melting temperature of at-PS/iso-PS/CS₂ gels with variation in mixture components. These results suggest that not crystallization, but chemical structure and interactions due to the side groups have more important roles for the gelation of PS/CS₂ solution. Enthalpy change of the network junction points of P α MS/CS₂ gels was determined to be higher than that of at-PS/CS₂ and iso-PS/CS₂ gels, suggesting that there is the stronger junction point for P α MS/CS₂ gels than at-PS/CS₂ gels.

KEY WORDS Thermoreversible Gelation / Gels / Chemical Structure / Polystyrene / Poly(α -methyl)Styrene / Carbon Disulfide /

Solutions of polymers transform usually into thermo-reversible gels on cooling. It was believed that only crystallizable and stereo-regular polymers can form thermoreversible gels. The discovery of Wellinghoff *et al.*¹ and Tan *et al.*² that non-crystallizable atactic polystyrene solutions form physical gels has attracted much attention. However, the nature and structure of gel junction points are so complex that they still remain unsolved uniquely. Particularly, in the case of crystallizable polymers, it is difficult to check whether gelation is induced directly by crystallization, or by some other mechanism.

In previous papers,^{3–5} the melting behavior of atactic- and isotactic-polystyrene-carbon disulfide (at- and iso-polystyrene (PS)/CS₂) gels was investigated and iso-PS/CS₂ gels showed two endothermal DSC peaks while at-PS/CS₂ gels one peak. The low temperature peak was considered due to the melting of gel junction points and the high temperature peak, to the melting of crystals. No definite difference between the gelation mechanism of iso- and at-PS/CS₂ system strongly suggested that gelation of iso- and at-PS/CS₂ solutions occurred independently of crystallization. Moreover, the gel melting temperature of iso-PS/CS₂ gels system was slightly higher than that of at-PS/CS₂ gels at the same polymer molecular weight and concentration suggesting similarity in the structure of the gel network junction points.

Based on above results, the gelation phenomenon is very similar in both at- and iso-PS/CS₂ systems, and it is expected that the gelation of PS/CS₂ system is not caused by crystallization, but probably the interaction of the side phenyl group. In this study, to elucidate the mode of PS/CS₂ gelation, a non-crystallizable Poly(α -methyl) styrene (P α MS) which has the side group -CH₃ in the chain more than PS was used to make gels in the

solvent of CS₂. The gelation was investigated to compare with at- and iso-PS/CS₂ systems. The gel melting temperature and enthalpy change of the gel network junction points for P α MS/CS₂ system was determined. The effect of chemical structure of molecules on gelation is discussed.

EXPERIMENTAL

Materials

P α MS sample used in this study was obtained from Aldrich Chemical Co., Inc. The molecular weight of the sample is $M_w = 113000$. PS sample ($M_w = 210000$) was obtained from Wako Pure Chemical Industries Co., Ltd. CS₂ was high purity grade chemicals and dried over molecular sieves before use.

Measurement of Gel Melting Temperature

P α MS/CS₂ solutions whose polymer concentrations varied from 40 g l⁻¹ to 270 g l⁻¹ were prepared in sealed glass tubes of an inner diameter of 12mm. After the polymer was dissolved at room temperature, the glass tube with solution was quenched in a freezer kept at constant temperature for one week to make gels. The gel was defined as the state where no flow occurred when the test tube was kept inverted for one day. The gel melting point was determined using a so-called test tube upside-down method. The test tube with gel after being kept upside down in a well-stirred methyl-ethyl alcohol mixing bath was heated at the rate of 0.5°C min⁻¹. The temperature where the meniscus began to flow was defined as the melting temperature of gel, T_m^g .

Preparation of Blend Gel Samples

An appropriate amounts of P α MS/at-PS and at-PS/iso-PS were sealed in glass tube with solvent CS₂, and heated in the boiled water bath for a long time until the polymer samples completely dissolved. The homog-

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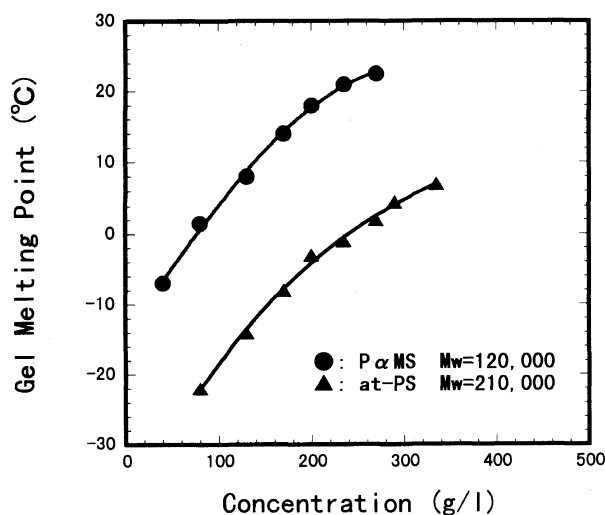


Figure 1. Dependence of gel melting temperature on polymer concentration for at-PS/CS₂ and PαMS/CS₂ gels.

enous solutions were put in a freezer of -20°C to make gels. The gel melting temperature was the same as that of PαMS/CS₂ gels.

RESULTS AND DISCUSSION

Solutions of non-crystallizable polymer PαMS in CS₂ formed gels on cooling and the gels converted to sols on heating. This gel-sol transition was thermoreversible. PαMS/CS₂ solutions formed gels as well as those of at-PS/CS₂ solutions at relatively low temperature. The polymer concentration dependence of the gel melting temperature is illustrated in Figure 1. The melting temperature moves to higher temperature with increasing polymer concentration. The gel melting temperature T_m^g of PαMS/CS₂ is much higher than that of at-PS/CS₂, about 20°C at the same polymer concentration, although the molecular weight of PαMS is slightly less than that of at-PS. However, the gel melting temperature T_m^g of at- and iso-PS/CS₂ systems was nearly the same at the same polymer molecular weight and concentration. The chemical structures, in particular side groups of polymer thus appear essential to the gelation of non-crystallizable polymers. The mobility and size of side group in the chain should be related to gelation.

To get a clear-cut understanding of the differences in the gel melting temperatures of PS/CS₂ and PαMS/CS₂ gels, it is important to recognize side group interactions between the PαMS and at-PS in CS₂. PαMS was blended with at-PS in CS₂ and the gelation of at-PS/PαMS/CS₂ mixture system was investigated.

Figure 2 illustrates the gel melting temperature of at-PS/PαMS/CS₂ mixture system against the polymer weight fractions of PαMS. The gel melting temperatures of at-PS/PαMS/CS₂ blend systems varied between the gel melting temperatures of at-PS/CS₂ and PαMS/CS₂ systems, and increased with PαMS weight fraction. The plot indicated a sigmoid curve as shown in Figure 2. The gel melting temperature of the blend system changed gradually at low and high PαMS fractions in gels of the mixtures. At low weight fraction of PαMS, the gel melting temperature of the mixtures was close to that of at-PS/CS₂ systems. The gel melting temperature was close

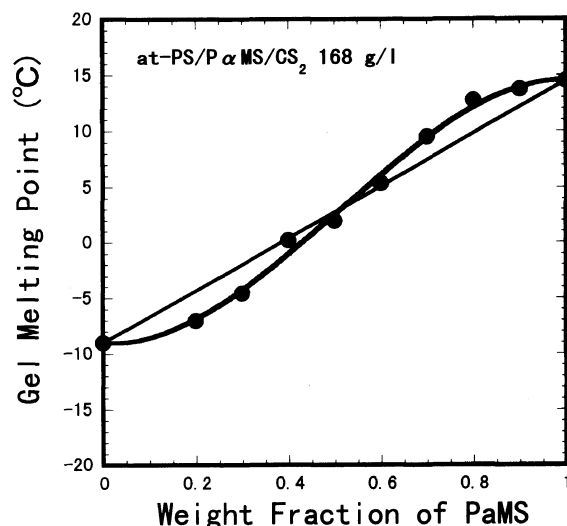


Figure 2. Dependence of gel melting temperature on polymer concentration for at-PS/PαMS/CS₂ system.

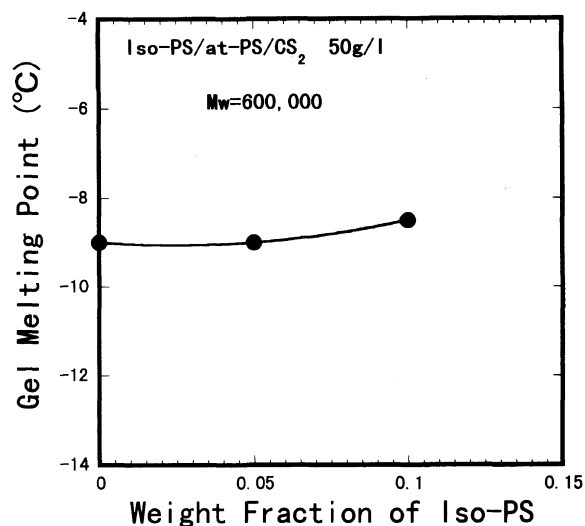


Figure 3. Dependence of gel melting temperature on polymer concentration for at-PS/iso-PS/CS₂ system.

to that of PαMS/CS₂ systems at high weight fraction of PαMS. It is expected that the network junction points of the mixture gels are mainly composed of at-PS chains at the high at-PS weight fraction, and composed of PαMS chains at the high PαMS weight fraction in the mixtures. Furthermore, when the blend components of at-PS and PαMS were close in the mixtures, the gel melting temperature of the mixtures had a linear additivity behavior and might be described below:

$$T_{m^g}^{\text{blend}} = X_A T_{m^g}^{\text{at-PS}} + X_B T_{m^g}^{\text{P}\alpha\text{MS}} \quad (1)$$

where X_A , X_B are the weight fractions of at-PS and PαMS in the blends. The gel network junction points of the mixtures should thus be composed of at-PS and PαMS mixed chains when the blend components of at-PS and PαMS were close in the mixtures.

The gel melting temperature of at-PS/iso-PS/CS₂ mixture gels is plotted against polymer concentrations in Figure 3. Almost no change was found in the gel melting temperature of the at-PS/iso-PS/CS₂ blends systems with increasing iso-PS weight fraction. This is certainly reasonable considering no obvious difference in the

gel melting temperature between the at-PS and iso-PS/CS₂ gels and the same chemical structure of at- and iso-PS.³

No difference in gel melting temperature for the at-PS, iso-PS and at-PS/iso-PS/CS₂ gels means that the gel network junction points due to the chain-chain interaction in CS₂ are similar. The difference of the gel melting temperature in at-PS, P α MS and at-PS/P α MS/CS₂ gels strongly signifies that the chain-chain interactions in the gel junction points depend on chemical structure. Chain-chain interactions in the gels should mainly be related to the phenyl rings of the side group, and interactions between the side groups induced differences of the gel network junction points. Thus not crystallization, but chemical structure and interactions are apparently important to gelation of PS/CS₂ solutions.

According to Eldridge and Ferry,⁶ the dependence of T_m^g on the polymer concentration C is,

$$\ln C = \frac{\Delta H}{RT_m^g} + \text{Const.} \quad (2)$$

where C is concentration given as grams per liter unit. ΔH corresponds to the enthalpy change of a mol of potential network junction points.^{7,8} R is a gas constant. This relationship is derived under the assumption that two moles of cross-linking loci combine to form one mole of cross-linking making a network and that the rates of formation and decomposition of cross-linking are equilibrated. The equation is applicable to at-PS gels by Tan *et al.*²

Based on eq 2, a plot of the reciprocal of T_m^g for P α MS/CS₂ system against logarithmic polymer concentration should give a straight line, as illustrated in Figure 4. A good straight line was obtained as same as for at-PS gels. The linear relationship obtained from eq 2 implies that the present data satisfy the Eldridge-Ferry's relation and the concentration dependence of gel-melting point for P α MS/CS₂ gels can be presented well by this type of plot. ΔH , determined from the slope in Figure 4, was 9 kcal mol⁻¹.

ΔH of various polymers estimated from eq 2 are summarized in Table I. ΔH of poly(vinyl alcohol) (PVA)/water gels is considered to correspond to two or four hydrogen bonds.^{9,10} Poly(vinyl chloride) (PVC)/dioxan gel is formed by chain associations due to hydrogen bonds.¹⁰ In at-PS/CS₂ gel no hydrogen bonding is formed, and ΔH of at-PS/CS₂ gel moves from 6 kcal mol⁻¹ to 10 kcal mol⁻¹ with increasing molecular weight. ΔH of crystallizable iso-PS/CS₂ gel is the same as that of non-crystallizable at-PS/CS₂ gel at the same polymer molecular weight.³ The structures of the gel network junction points of at- and iso-PS/CS₂ gel systems thus appear similar.

ΔH of P α MS/CS₂ gels is higher than that of at-PS/CS₂ gels at the same polymer molecular weight, suggesting that the bulky side group plays an important role in the gelation of PS/CS₂ systems.¹⁵ The gelation of long side chain poly(alkyl acrylates) has been reported¹²⁻¹⁴ closely related to the chemical structures of side chains.

The gelations of PS/CS₂ systems may be induced by interactions between the side groups of two or more polymer chains. The bulkier the side group in the chain,

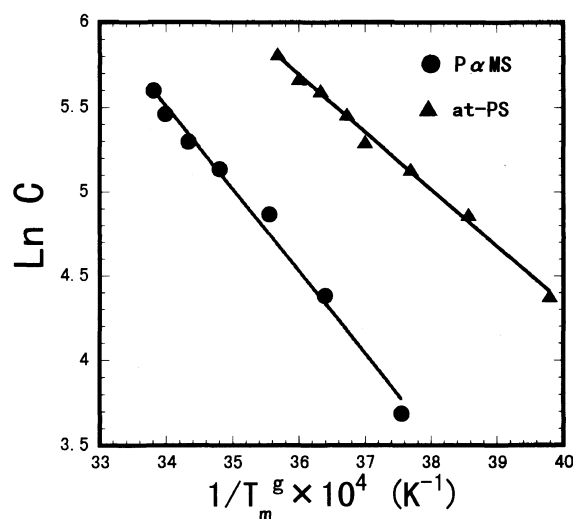


Figure 4. Relation between the reciprocal of gel melting temperature and logarithm of polymer concentration for at-PS/CS₂ and P α MS/CS₂ systems.

Table I. Gelation enthalpy of various PS/CS₂ estimated from Eldridge-Ferry equation

Polymer/solvent	ΔH (kcal mol ⁻¹)
P α MS/CS ₂ ($M_w = 113000$)	9
at-PS/CS ₂ ($M_w = 210000$)	6
at-PS/CS ₂ ($M_w = 600000$)	10
iso-PS/CS ₂ ($M_w = 600000$)	10

the more chain rigidification may easily occur, which makes the interactions between side groups easier in the CS₂ solvents. If interactions of the phenyl rings between two PS chains lead to as stacking of the chains in the low temperature, the stacking chains should function as network junction points, and the solvent molecules should be located between chains. This possibility in P α MS/CS₂ gels should be expected higher than that in at- and iso-PS/CS₂ gels. For P α MS, because the chain is more rigid than that of PS, interactions like chain stacking between phenyl rings should be easily occurred in longer sequence. This induces stronger gel network junction points and higher melting point of P α MS/CS₂ gels.

Investigation of the molecular mobility and molecule structure in gel state is needed.

CONCLUSIONS

(1) P α MS/CS₂ solutions form thermoreversible gels. The gel melting temperature was much higher than that of at-PS/CS₂ gels to be about 20°C at the same concentration and molecular weight, implying that the chemical structure and rigidity of the chains have significant influence on gelation.

(2) Mixed solutions of at-PS/P α MS/CS₂ and at-PS/iso-PS/CS₂ form thermoreversible gels. The melting temperature of the at-PS/P α MS/CS₂ gels shifts to higher temperature with increasing weight fraction of P α MS. In contrast, no obvious change was observed in the melting temperature of at-PS/iso-PS/CS₂ gels with varying component of the mixtures. Thus not crystallization, but

chemical structure and interactions are more essential to the gelation of PS/CS₂ solutions.

(3) Enthalpy change of the network junction points of P α MS/CS₂ gels is higher than that of at-PS/CS₂ and iso-PS/CS₂ gels, suggesting that there stronger junction points for P α MS/CS₂ gels than at-PS/CS₂ gels.

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