Thermoreversible gelation mechanism of polystyrene–carbon disulphide solutions*

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(*Received 13 November 1989; revised 21 February 1990; accepted 27 February 1990*)

The mechanism of the sol–gel transition in atactic and isotactic polystyrene–carbon disulphide systems was studied. It was found that iso-PS–CS_2 solutions formed gels at low temperatures as well as those of at-PS–CS_2. The gel melting point of iso-PS–CS_2 was a little higher than that of at-PS–CS_2 at the same polymer molecular weight and concentration. The calorimetric observations confirmed that the sol–gel transition was of the first order. The sol–gel transition point shifted to higher temperature with increasing gelation temperature and time, implying that the stability of junction points in gels increased with gelation temperature and time. Iso-PS–CS_2 gels showed two endothermal d.s.c. peaks while at-PS–CS_2 gels showed one peak: the low temperature peak was due to the gel melting and the high temperature peak was due to the crystal melting in the gel. The heat of gel melting per polymer was about 1 J g^{-1} which was equal to that of at-PS–CS_2 gels. It was difficult to find any definite difference between the gelation mechanisms of at- and iso-PS–CS_2 systems, except that crystals coexisted in iso-PS gel networks. This led us to conclude that the gelation of iso-PS–CS_2 solutions took place independently of crystallization.

(Keywords: atactic; isotactic; polystyrene; carbon disulphide; sol–gel transition; d.s.c.; heat of gel melting; junction point)

INTRODUCTION

Many polymer solutions form thermoreversible gels on cooling. These comprise three-dimensional networks of polymer chain cross-linked by physical bonds[1,2]. Several mechanisms have been proposed as the origins of the thermoreversible gel networks[3–11]. In the case of crystallizable polymers, it is difficult to check whether gelation is induced directly by crystallization, or by some other mechanism.

Wellinghoff *et al.*[12,13] and Tan *et al.*[14,15,16] found that non-crystallizable atactic polystyrene (at-PS) formed thermoreversible physical gels in many solvents, and pointed out that both entanglement of polymer chains and liquid–liquid phase separation were not necessary for the gelation of at-PS–CS_2 solutions. To check the effect of crystallizability on gelation, they investigated the gelation of a series of chlorinated polyethylenes (PE) in toluene[17,18]. The polymers had a wide span from 'non-crystallizable' to 'highly crystallizable' depending on the chlorine content and distribution. They plotted the enthalpy of gelation obtained from Eldridge–Ferry's relation as a function of the heat of melting of their bulk state measured by d.s.c., and found the plot formed a single straight line regardless of the chlorine distribution. From the plot they estimated a gelation enthalpy of 24 kJ mol^{-1} for the assumed non-crystallizable specimen. Since the enthalpy of at-PS–CS_2 gel is nearly equal to that of non-crystallizable chlorinated PE in toluene, they supposed that the junction point in at-PS gels was like a precursor of a fringed micellar junction.

The correspondence of at-PS to chlorinated PE is not always clear because of their different chemical structures and solvents used. On the other hand, Francois *et al.*[19] studied the endotherm of at-PS–CS_2 gels in d.s.c. and suggested that a polymer–solvent complex or a stoichiometric compound might be formed in the gels.

In our previous paper[20], the gelation kinetics of at-PS was studied and the critical gelation temperature was about 13°C lower than the gel melting temperature at a given polymer concentration. This hysteresis showed clearly that the gelation had a rate process.

In this study, the thermodynamics of at-PS–CS_2 gels were investigated to elucidate the mode of gelation, and then the gelation of iso-PS–CS_2 was studied showing that iso-PS–CS_2 solution formed a gel at temperatures as low as those at which at-PS–CS_2 formed a gel. The properties of both at- and iso-PS–CS_2 gels are compared to discuss their mechanisms of gelation.

EXPERIMENTAL

Materials

Two at-PS samples ($M_w = 600\,000$, $M_w/M_n = 1.1$ and $M_w = 210\,000$, $M_w/M_n = 1.7$) were obtained from Nishio Kougyo Ltd and Wako Pure Chemical Industries Ltd, respectively. An iso-PS ($M_w = 600\,000$, $M_w/M_n = 1.9$) was obtained from Polymer Laboratories Ltd. The high-purity-grade CS_2 was treated over molecular sieves before use.

Measurement of gel melting point

At-PS–CS_2 solutions with polymer concentrations varying from 10 g l^{-1} to 100 g l^{-1} were prepared at room temperature in sealed glass tubes, inner diameter 12 mm. Once the polymer had dissolved, each solution was left at room temperature for three days for homogenization. The solution was then quenched for one week in a freezer at a given temperature to form a gel.The gel state was

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* Presented in part at the 36th Meeting of the Society of Polymer Science, Japan, October 1987

0032-3861/91/030479-05

defined as that where no flow occurred when the test tube was inverted.

As it was difficult to dissolve iso-PS in CS_2 at room temperature, the sealed tube containing an appropriate amount of polymer and solvent was heated in boiling water until the polymer completely dissolved. In this investigation iso-PS–CS_2 homogeneous solution could be obtained only at concentrations less than 40 g l^{-1}.

The gel melting point was determined by keeping the test tubes upside down in a well stirred ethanol–methanol bath and heating at a rate of 0.2°C min^{-1}. The temperature at which the meniscus began to flow was defined as the gel melting point $T_m{}^g$.

Differential scanning calorimetry

D.s.c. measurements of gels were carried out using Seiko DSC560 and DSC100 equipped with a data analysis station for the baseline correction and calculation of the transition heat. About 20 mg of at-PS–CS_2 solution was put in an aluminium sample pan and immediately sealed and weighed. The pan was also weighed after the measurement to confirm that no evaporation of solvent took place during d.s.c. measurement. The low temperature cover was put on the top of sample holders, and all experiments were carried out under a constant flow of dry nitrogen. Liquid nitrogen was used as coolant. After being kept at a fixed gelation temperature for a given time, the d.s.c. run started at a constant rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the gel melting point $T_m{}^g$ on the polymer concentration for at- and iso-PS–CS_2 gels. The $T_m{}^g$ moves to higher temperature with increasing polymer concentration, and the $T_m{}^g$ of iso-PS gels is only about 3–4°C higher than that of at-PS–CS_2 gels at the same polymer concentration.

On the other hand, according to Eldridge and Ferry[21], the dependence of $T_m{}^g$ on the polymer concentration C is given by:

$$\ln C = \frac{\Delta H}{RT_m{}^g} + \text{constant} \qquad (1)$$

where C is in g l^{-1}, ΔH is the enthalpy change of junction point, and R is the gas constant. This relationship is derived by assuming that two moles of cross-linking loci combine to form one mole of cross-link making a network and that the rates of formation and decomposition of cross-links are equilibrated. Tan *et al.*[14] have already shown that the equation is applicable to at-PS–CS_2 gels.

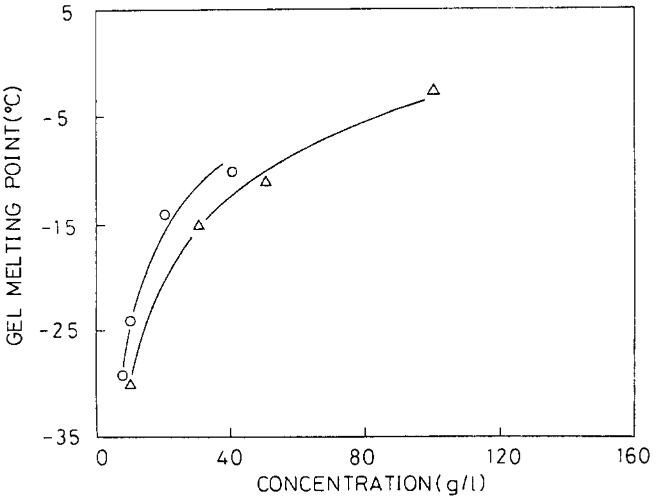

Figure 1 Dependence of gel melting temperature on polymer concentration for: ○, iso- and △, at-PS–CS_2 gels, $\bar{M}_w = 6 \times 10^5$

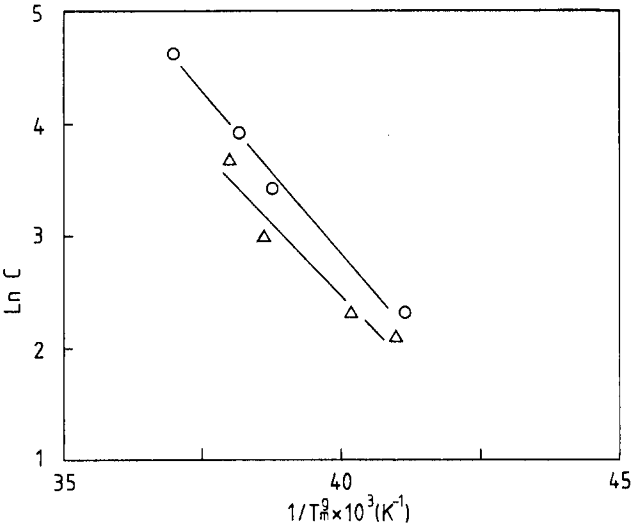

Figure 2 Relation between the reciprocal of gel melting temperature and the logarithm of polymer concentration for: △, iso- and ○, at-PS–CS_2 systems. $\bar{M}_w = 6 \times 10^6$

Table 1 Gelation enthalpy of various polymer–solvent systems estimated from Eldridge–Ferry's equation

Polymer–solvent	ΔH (kJ mol^{-1})
Chlorinated PE–toluene	50–420[17]
PVA–water	50–84[22]
PVC–1,4-dioxan	50[10]
Polyphosphazene–water	50[23]
Iso-PS–CS_2	42
At-PS–CS_2	42

The reciprocal of gel-melting point for at- and iso-PS–CS_2 systems is plotted as a function of logarithmic polymer concentration in *Figure 2*. Linear relationships are obtained for both at- or iso-PS–CS_2 gels. ΔH, determined from the slopes in *Figure 2*, is 42 J mol^{-1} for both at- and iso-PS–CS_2 gels.

Values of ΔH of various polymers estimated from equation (1) are summarized in *Table 1*. According to Tan *et al.*[17] the ΔH of the chlorinated polyethylene–toluene system is due to formation of a precursor of a fringed micellar junction. The ΔH of PVA–water gels has been supposed to correspond to two or four hydrogen bondings[22]. The PVC–dioxan gel is formed by chain associations due to hydrogen bonds[10]. In the case of a non-crystalline polyorganophosphazene–water gel, the ΔH corresponds to two or three hydrogen bonds[23]. In at- and iso-PS–CS_2 gels no hydrogen bonding is formed, and the ΔH of at-PS–CS_2 gel may be related to the association of short chain segments[18]. It is noticed that the ΔH of crystallizable iso-PS–CS_2 gel is the same as that of non-crystallizable at-PS–CS_2 gel.

The dependence of gel melting on the temperature and time of gelation was examined by d.s.c. at an earlier stage of gelation. The d.s.c. curves in *Figure 3a* were obtained by the following procedure: a pan containing at-PS–CS_2

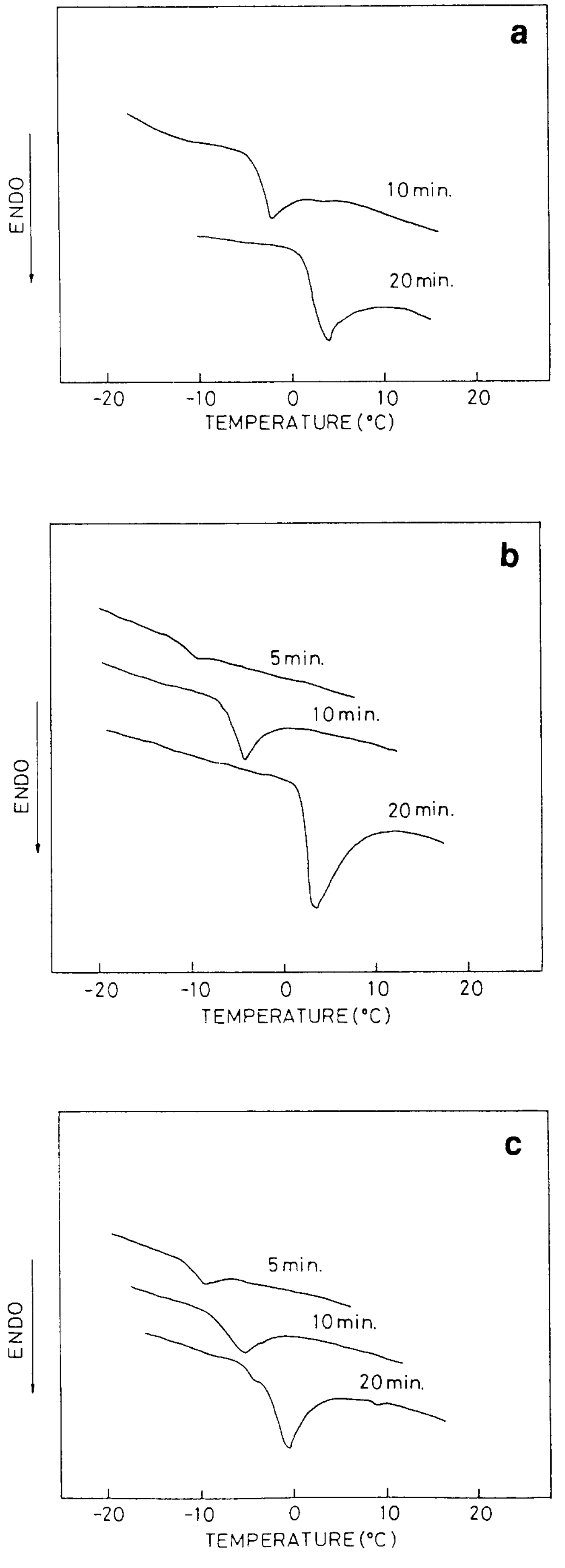

Figure 3 D.s.c. thermograms of at-PS–CS$_2$ gels at various gelation times: (a) gelation at -30°C; (b) at -50°C; (c) at -70°C. Heating rate: 20°C min^{-1}. $\bar{M}_w = 21 \times 10^4$; polymer concentration = 250 g/l

solution was cooled and kept at -30°C for 10 min to make gel, then heated up to 25°C at a heating rate of 20°C min^{-1}. After being held at 25°C for 5 min, this cooling-gelation-heating procedure was repeated changing the gelation time. The cases where the pan was cooled at -50°C and -70°C for various gelation times are shown in *Figures 3b,c*. The appearance of transition heat indicates that sol–gel transition of at-PS–CS$_2$ is of the first order, as was already reported by Francois *et al.*[19].

The most important result in *Figure 3* is that the d.s.c. endothermic peak depends strongly upon gelation time at the early stage of gelation at a fixed temperature; the longer the gelation time, the more the peak shifts to high temperature, accompanying an increase in the gel melting heat. Furthermore, the dependence of the gel melting point on the gelation temperature is different at different stages of gelation as shown in *Figure 4*. In *Figure 4a* the d.s.c. curve shifts to higher temperature with decreasing gelation temperature at a gelation time of 5 min. In *Figure 4b* for 10 min gelation, the peak shifts to higher temperature with increasing gelation temperature. This tendency is more explicit for longer gelation time.

These results are summarized in *Figure 5* where the relations between the gel melting point and gelation temperatures are shown at various gelation times. The shift of $T_m{}^g$ is large at high gelation temperature. The increase of $T_m{}^g$ with gelation time implies that the gel cross-linking points grow larger with gelation time at the early stage of gelation. The growth of the gel cross-linking points means the increase in the number of chain segments participating with a network junction point, accompanying the increase of the number of chemical units in each segment. The increase in the heat of gel melting with gelation time is due to the growth of each junction point and also to the increasing number of junction points.

When the gelation time is long enough for gelation to reach equilibrium, the gel melting point should no longer depend upon gelation time. However, the data at 20 min (*Figure 5*) implies that the gel melting point of a given solution might depend on the gelation temperature even at the last stage of gelation; the higher the gelation temperature, the higher the gel melting point.

It is to be expected that the junction points in gels prepared at higher temperature must endure stronger thermal movements of polymer segments, compared with those prepared at lower temperatures. This may result in higher melting points for gels prepared at high temperature.

The fact that the effect of gelation temperature on the gel melting point depends on the gelation time may be explained by the following reasons: (1) the rate of gelation increases with decreasing temperature as we have already shown; (2) each junction point grows, increasing its stability with time; and (3) the melting point of gels prepared at higher temperatures should be higher than that of gels prepared at low temperature.

The heat of gel melting per polymer obtained from d.s.c., was as little as about 1 J g^{-1} at gelation temperature -50°C and time 20 min.

Similar d.s.c. experiments were carried out for the iso-PS–CS$_2$ system and the results are shown in *Figure 6*. The d.s.c. peak had the same dependence on the gelation temperature and time as did the at-PS–CS$_2$ system, but two endothermal peaks appeared in the case of iso-PS–CS$_2$, while only one peak appeared with

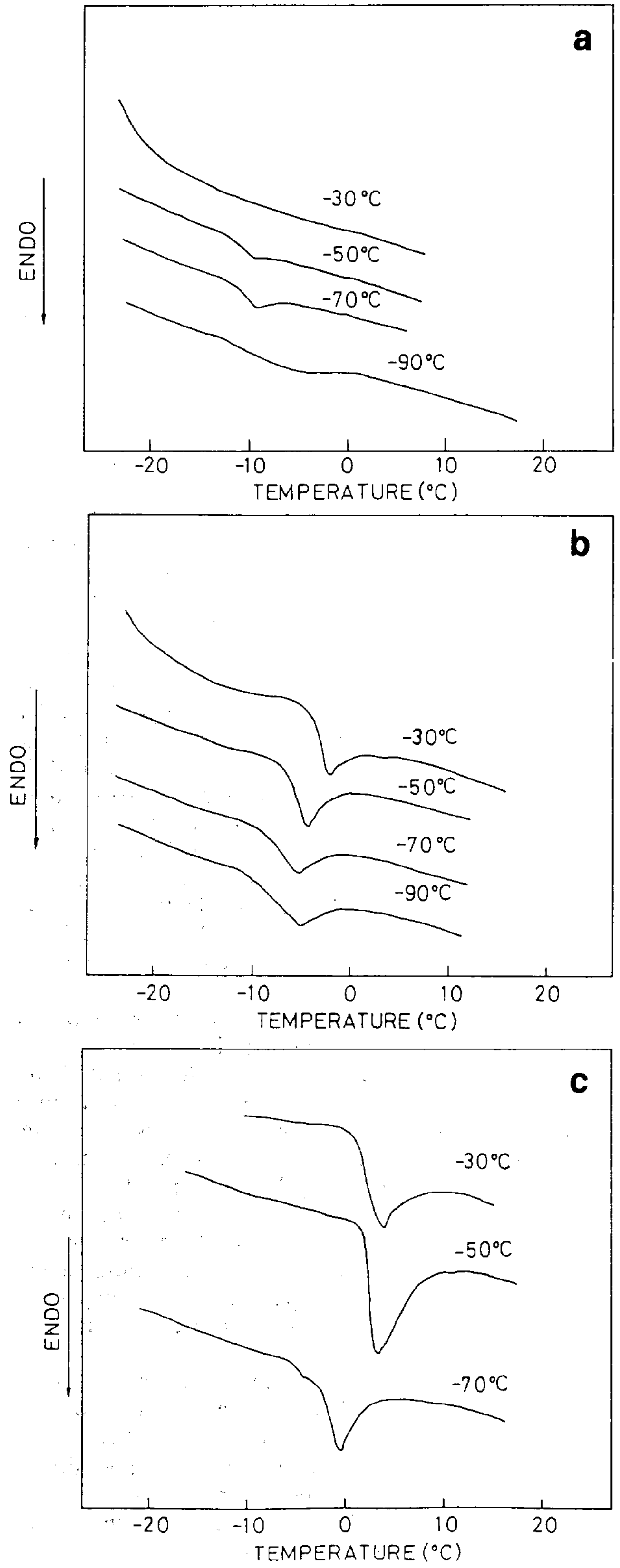

Figure 4 D.s.c. thermograms of at-PS–CS_2 gels at various gelation temperatures: (a) for gelation time 5 min; (b) 10 min; (c) 20 min. Heating rate: 20°C min^{-1}. $\bar{M}_w = 21 \times 10^4$; polymer concentration = 250 g/l

at-PS–CS_2 gels. The lower temperature peak is not clear at -30°C gelation, but is obvious in the gels formed at -50°C. The lower temperature peak can be attributed to the melting of the gel network because the peak

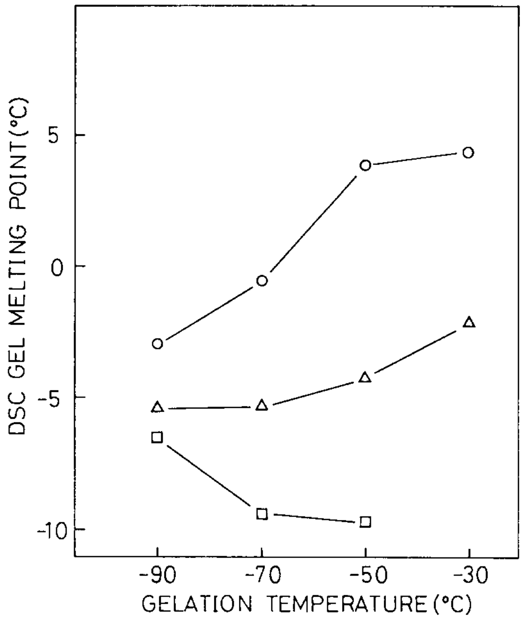

Figure 5 Dependence of d.s.c. peak temperature on the gelation temperature for various gelation times. ○, 20 min; △, 10 min; □, 5 min

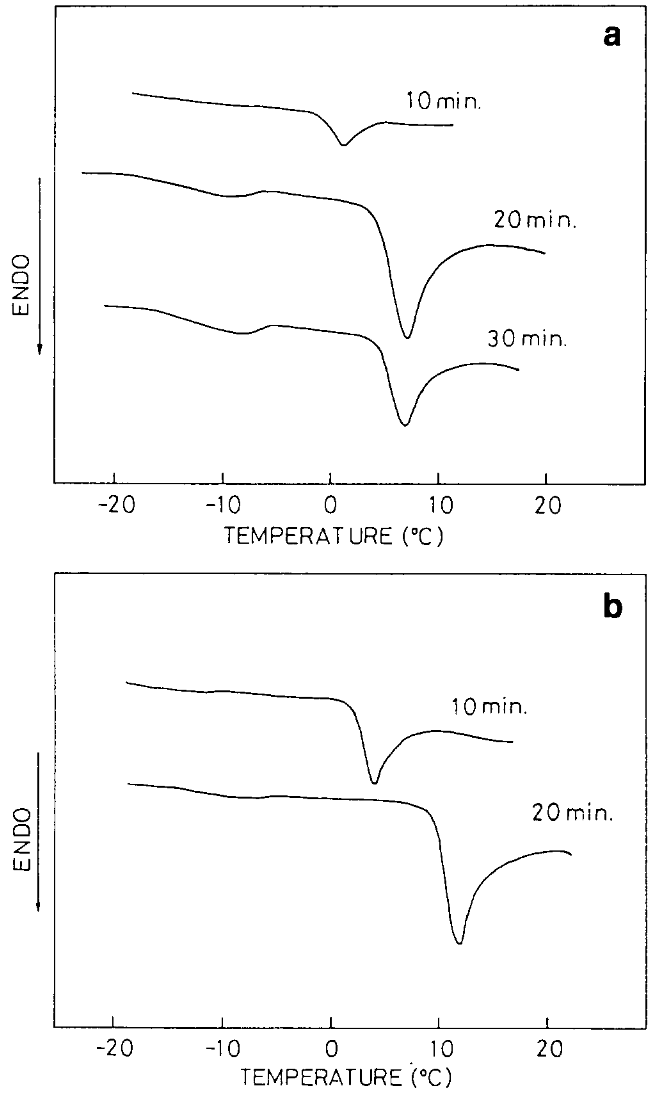

Figure 6 D.s.c. thermograms of iso-PS–CS_2 gels for various gelation times: (a) gelation at -50°C; (b) -30°C. Heating rate: 20°C min^{-1}; polymer concentration = 30 g/l

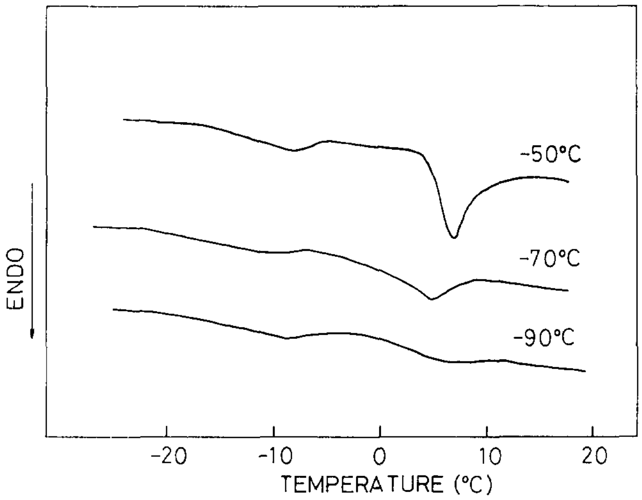

Figure 7 D.s.c. thermograms of at-PS–CS_2 gels for various gelation temperatures for gelation time 30 min. Heating rate: 20°C min^{-1}; polymer concentration = 30 g/l

temperature is the same as the gel melting point measured in the inverted tube method as shown in *Figure 1*.

The heat of gel melting per polymer, estimated from the low temperature peak, is the same as that for at-PS–CS_2—about 1 J g^{-1}. On the other hand, the high temperature peak corresponds to the melting of crystal in the gel, which was confirmed by observation of the test-tube with gels. The solution was somewhat turbid even after the gel melted but became clear at room temperature.

Figure 7 shows the dependence of d.s.c. thermograms on gelation temperature at gelation time 30 min. Here we can see the same dependence of gel melting peak on the temperature as that in the at-PS–CS_2 system.

These results suggest that the mechanisms of gelation of at- and iso-PS–CS_2 systems are very similar and independent of crystallization. However, Atkins *et al.*[24] found a new type of crystal, different from the usual 3_1 structure in the iso-PS decalin solution gels and considered that the gel network was formed by the new crystal as a junction point of fringed micellar crystal type. In our study, at-PS would not be expected to form crystals in the solutions. Furthermore, we have confirmed that iso-PS–CS_2 forms no new type of crystal using X-ray and *FT*i.r. and only a usual three-fold screw crystal exists.

SUMMARY

The melting point of at-PS gel shifts to higher temperature with increasing gelation temperature and time, implying that junction points grow with gelation time, and the junction points in gels formed at higher temperatures are more stable.

Iso-PS–CS_2 solutions form gels at low temperatures just as at-PS–CS_2 solutions do. The gel melting point of iso-PS–CS_2 is slightly higher than that of at-PS–CS_2 at the same polymer molecular weight and concentration, suggesting a similarity in the structure of gel network junction points.

Iso-PS–CS_2 gel shows two d.s.c. endothermal peaks corresponding to the melting of the gel and of crystals formed in the iso-PS–CS_2 solution. There is no indication of a substantial difference between gelation mechanisms of at- and iso-PS–CS_2 solutions, although in the case of iso-PS–CS_2, additional crystallization takes place in the gel network.

ACKNOWLEDGEMENTS

We thank Professor Hashimoto of the Tokyo Institute of Technology for allowing us to use the d.s.c. apparatus. We are also grateful for the help of Miss Nishimoto at Seiko Denshi for d.s.c. measurements.

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