# Thermoreversible gelation of poly(vinylidene fluoride) in $\gamma$-butyrolactone solution

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Poly(vinylidene fluoride) gels were formed in $\gamma$-butyrolactone; the critical polymer concentration for gel formation was 4.5 g per 100 cm$^3$. Gelation was caused by liquid–liquid phase separation, even if solid–liquid phase separation by crystallization occurred in the late stage of gelation, as shown by the formation of transparent gel, a relatively small enthalpy of gel formation and the existence of two types of crystal structures. In the dried gel films many spherulites connected by tie molecules were observed by scanning electron microscopy; the existence of such tie molecules is likely to make the formation of the gel films possible.

**(Keywords: poly(vinylidene fluoride); $\gamma$-butyrolactone; thermoreversible gels; gelation time; gel melting temperature; crystallization)**

## INTRODUCTION

Thermoreversible physical gels constitute three-dimensional networks whose junction points consist of physical bonds, such as hydrogen bonds, and dipolar interactions between polymer chains other than covalent bonding, which is considered as chemical crosslinking between chains. Physical gelation of polymer solutions is generally considered to arise from liquid–liquid phase separation by spinodal decomposition, crystalline formation of the polymer chains and a hydrogen bonding type association of the polymer chains[1–9]. However, the nature and structure of junction points are so complex that they are still subjects of some controversy.

In the physical gels of crystalline polymers, it has been suggested that crystallization is not a necessary condition for gelation[10,11]. However, crystallization necessarily follows gelation in gels prepared from solutions of crystalline polymers. Whether crystallization occurs in solution before gelation or in the gel phase after gelation may be determined by investigating gels from polymers exhibiting polymorphism. Tanigami *et al.*[10] reported that four crystal modifications of isotactic poly(4-methyl-1-pentene) (P4M1P) were found on gelation from solutions; by the observation of these modifications the gel phase of P4M1P can be divided into several regions exhibiting different morphology, revealing the gel mechanism of P4M1P.

Poly(vinylidene fluoride) (PVDF), which is a piezoelectric polymer[12], has at least four crystal structures but there has been no report as yet on its gelation behaviour. In this study, the gelation mechanism of PVDF/$\gamma$-butyrolactone system will be investigated.

## EXPERIMENTAL

PVDF (Kureha Co.) with an intrinsic viscosity of 68 cm$^3$ g$^{-1}$ at 90°C in $\gamma$-butyrolactone solution was used. Solutions with various weight per cent concentrations, and using $\gamma$-butyrolactone as solvent, were prepared by dissolving the polymer at 90°C in sealed test-tubes. The gels were formed by cooling the hot solutions in sealed test-tubes to room temperature. The hot solutions were also poured into an aluminium tray at room temperature in order to form gel films and the solvent was allowed to evaporate for several weeks from the gel films under ambient conditions. As a result, dried gel films were obtained.

Viscosity was measured with a Canon-Fenske viscometer at 90°C using $\gamma$-butyrolactone solutions.

Gel melting temperature ($T_m^g$) was determined from the peak temperature of the endothermic curve measured by differential scanning calorimetry (d.s.c.) using a liquid sample pan at the heating rate of 20°C min$^{-1}$.

A test-tube tilting method was used for measuring the gelation time ($t_{gel}$), which was defined as the time taken from the instant when the test-tube was put in the bath at a fixed temperature to the gelation.

Sol–gel transition temperature was determined by investigating the state of solution by the test-tube tilting method after the hot solutions were kept for 48 h at a fixed temperature.

X-ray diffraction and scanning electron microscopy (SEM) were used to investigate the crystal structure and the morphology of dried gel films.

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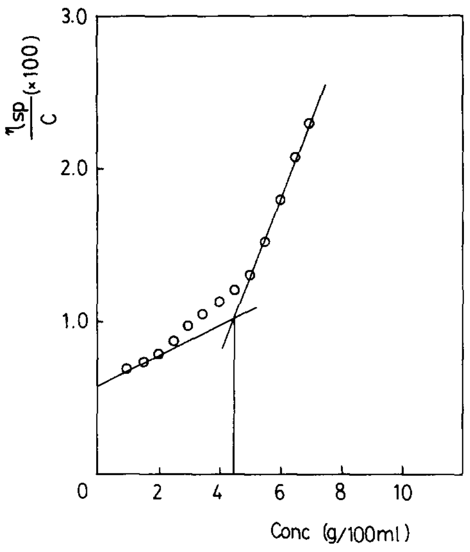

**Figure 1** Concentration dependence of reduced viscosity of PVDF solution at 90°C

## RESULTS AND DISCUSSION

All PVDF gels prepared by cooling hot solutions to a fixed temperature were transparent within measured ranges, regardless of gelation temperatures and polymer concentrations. During drying at room temperature, the transparency of the gels was dependent on the polymer concentration and drying time. Gels with less than 20 wt% polymer concentration became semitransparent and gels with more than 20 wt% concentration became turbid after 2 weeks of drying. Gel films gradually shrank as the drying time increased and the final size of dried gel films decreased to about half the diameter of the original gel sample after 10 weeks of drying. Dried gel films obtained from low concentration solutions had good mechanical properties and could be well drawn. But dried gel films obtained from solutions of relatively high concentration (more than 25%) had very low tensile strength and thus could not be drawn.

In order to determine the critical concentration for gel formation, the concentration dependence of the reduced viscosity was obtained as shown in *Figure 1*. Two reduced viscosity regimes appeared in low and high concentration regions and the critical concentration could be determined from the intersection of two lines; a value of 4.5 g per 100 cm$^3$ was obtained. This critical concentration is interpreted as the concentration at which solutions begin to form a coherent network[13] and gels could well be formed above this critical concentration.

*Figure 2* shows the d.s.c. thermograms of PVDF gels measured at a heating rate of 20°C min$^{-1}$. They show gel melting temperatures as endothermic peaks. Gel melting temperatures increase with increasing PVDF concentration. The phase diagram of PVDF/$\gamma$-butyrolactone gels is shown in *Figure 3*. Sol–gel transition temperature increases linearly with increasing polymer concentration, and at higher polymer concentration it is considered that sol–gel transition appears with gel melting. Eldridge and Ferry[3] proposed a relationship between melting temperature and polymer concentration:

$$\ln c = \text{constant} + \Delta H_m / R T_m^g \qquad (1)$$

where $c$ is the polymer concentration (g per 100 ml) and $\Delta H_m$ is the heat absorbed on formation of one mole of junction points. Equation (1) can be plotted as a linear relationship between $\ln c$ and the reciprocal of $T_m^g$. Experimental results on PVDF gels show a good linear relationship between $\ln c$ and $1/T_m^g$, as shown in *Figure 4*. From this, $\Delta H_m$ was calculated to be 12.47 kJ mol$^{-1}$. This value is very low, considering that PVDF is a crystalline polymer. It is generally regarded that gels from crystalline polymers have significantly higher $\Delta H_m$ than gels from amorphous polymers, which is illustrated in the case of atactic and isotactic polystyrene polymers[14]. Although PVDF is a crystalline polymer, the very low value of $\Delta H_m$ suggests that gelation from the PVDF solution is similar to that from an amorphous polymer solution.

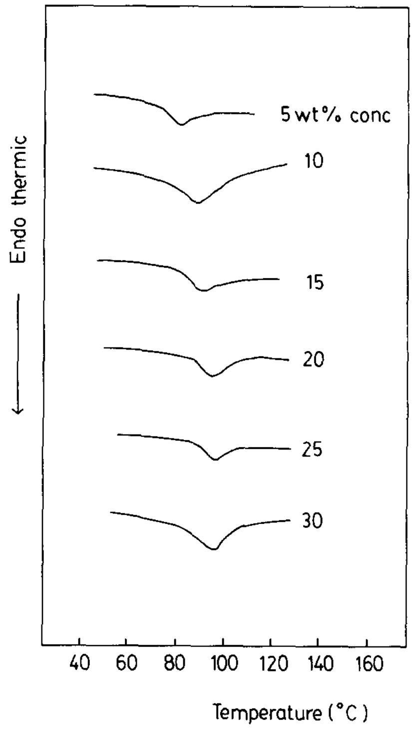

**Figure 2** D.s.c. thermograms of gels with various PVDF concentrations

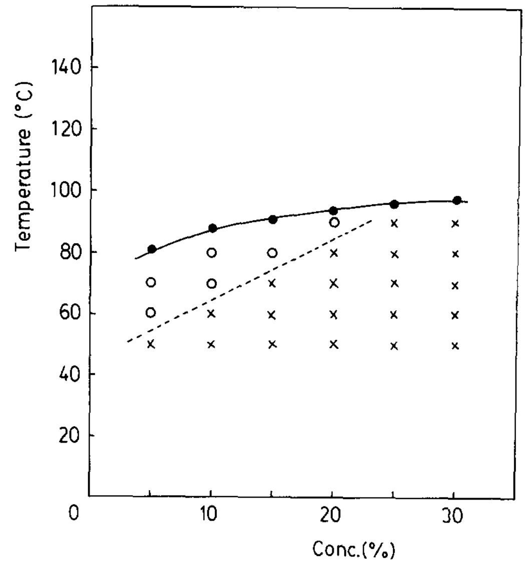

**Figure 3** Phase diagram of PVDF/$\gamma$-butyrolactone solution: —●—, gel melting temperatures; – – –, sol–gel transition temperatures (○, sol; ×, gel states)

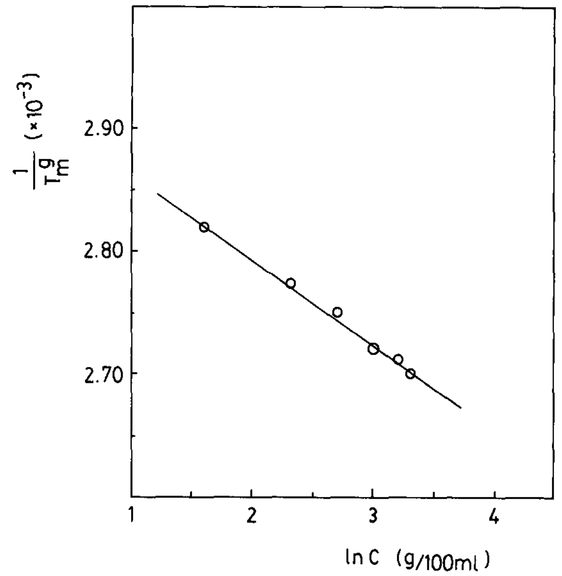

**Figure 4** Plot of reciprocal gel melting temperature *versus* the logarithm of PVDF concentration

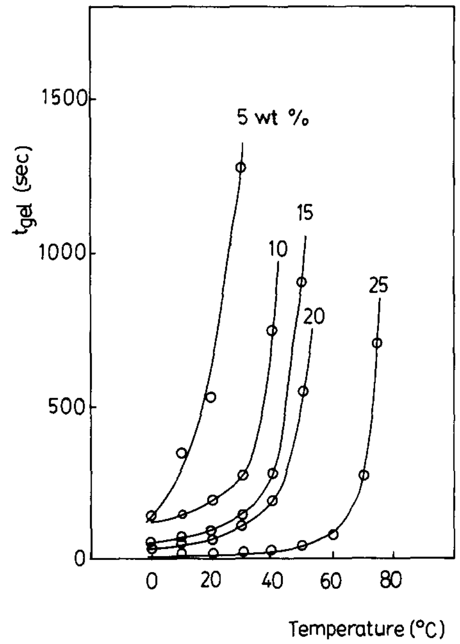

**Figure 5** Plot of gelation time *versus* gelation temperatures of gels with various PVDF concentrations

Gelation time of PVDF/$\gamma$-butyrolactone solution is plotted in *Figure 5* as a function of gelation temperature and concentration. Gelation time is highly dependent on gelation temperature and its temperature dependence is higher in the high temperature region. As the polymer concentration increases at a given gelation temperature, the gelation time decreases markedly. Since all the curves of gelation time–gelation temperature are similar with various polymer concentrations, they can be reduced to a master curve as in the study of Xie *et al.*[15] on atactic polystyrene gel. The resulting master curve is shown in *Figure 6*; it was obtained by using the gelation time–temperature curve of gel with 5 wt% polymer concentration as a standard. Assuming that the gelation rate obeys an Arrhenius relationship, the apparent activation energy ($\Delta E$) for the gelation was calculated as follows[15]:

$$1/t_{gel} = \text{constant} \times \exp(-\Delta E/RT) \qquad (2)$$

where $T$ is the gelation temperature. Since the plot of the logarithm of the gelation time against the reciprocal temperature was not linear, the activation energy should be represented as a function of supercooling temperature ($\Delta T$), that is, $T_m^g - T$. The $\Delta E$ is proportional to $(T_m^g - T)^{-1.6}$. This indicates that gel growth of PVDF in $\gamma$-butyrolactone is nearly three-dimensional; it has been reported[15] that in the case of poly(vinyl alcohol) aqueous solutions, gelation occurs three-dimensionally.

*Figure 7* shows the SEM picture of dried gels with 15 and 30 wt% polymer concentrations. Many spherulites linked by tie molecules are observed. Therefore, it is considered that the ability of the gel to form films arises from the existence of tie molecules between spherulites, as seen in the case of melt crystallization of crystalline polymers[16]. The crystal structures of such dried gel films were investigated by X-ray diffraction measurements as shown in *Figure 8*. X-ray diffraction patterns varied with polymer concentration in dried gel films. Dried gel films with PVDF concentration of 20 wt% or more showed a strong X-ray peak near $2\theta = 20.5°$, whereas films of 10 wt% or less showed an X-ray peak near $2\theta = 18.7°$ and $2\theta = 26°$ as well as $2\theta = 20.5°$. This indicates that dried gel films prepared from solutions with high PVDF concentration have crystals of form I and those prepared from solutions with low PVDF concentration have crystals of both forms I and II[17–20]. However, Grubb and Kearney[21] reported that dried gel film of PVDF prepared from 10 wt% $\gamma$-butyrolactone showed the isotropic form I crystal structure, but they did not give results for samples with any other concentration. This difference is likely to result from the difference in the molecular weight of PVDF. The existence of two crystal structures in this study is important in the mechanism of gel formation. It is considered that gels in high concentration solutions crystallize in one step but gels in low concentration solutions crystallize in two steps. Two-step crystallization[10] may result from liquid–liquid phase separation in the early stage of gelation and solid–liquid phase separation in two-phase gel at the

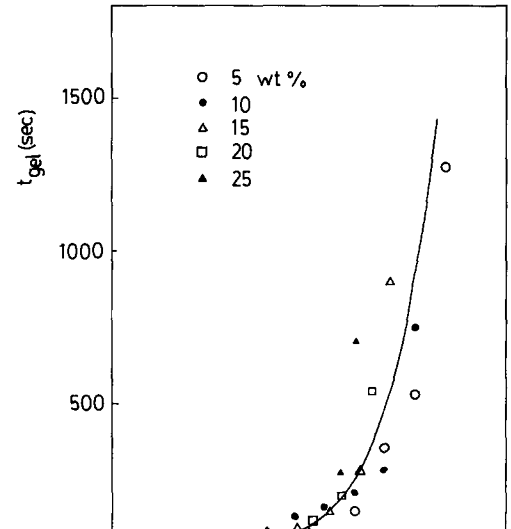

**Figure 6** Gelation time *versus* temperature curve obtained by shifting the relationship of gelation time and gelation temperature of gels with various PVDF concentrations

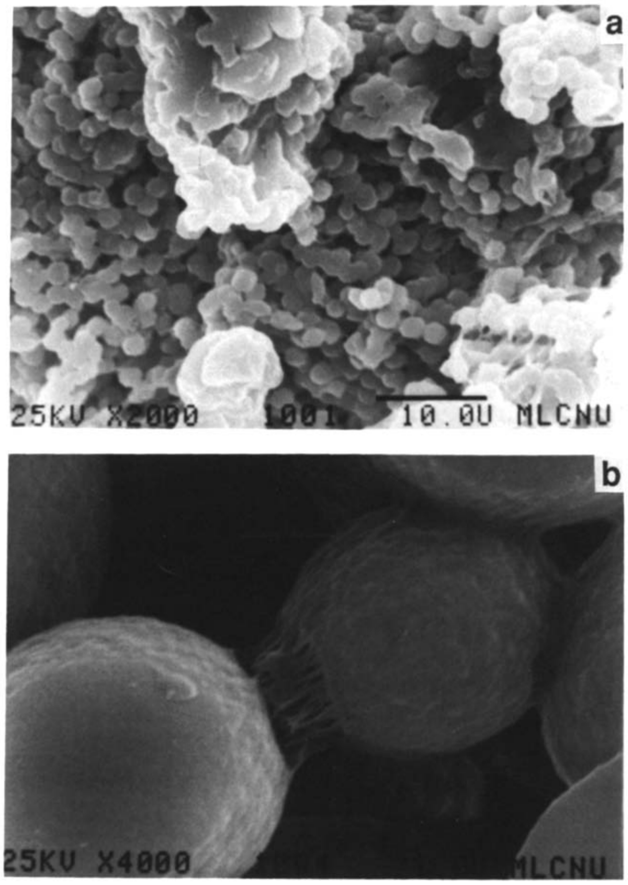

**Figure 7** SEM pictures of dried PVDF gels: (a) 15 wt% PVDF; (b) 30 wt% PVDF

final stage. Subsequently gelation is caused by some overlapping of polymer chains in the polymer-rich phase without crystallization. This means that crystallization is not necessary for gelation to occur. Consequently, results suggest that the gel mechanism of PVDF in $\gamma$-butyrolactone is liquid–liquid phase separation, as shown by gelation in the transparent state, a relatively small enthalpy of gel forming and the existence of two types of crystal structure.

## SUMMARY

Gelation occurred above a critical concentration of 4.5 g per 100 $cm^3$ of PVDF in $\gamma$-butyrolactone solutions, and the dried gel films prepared from solutions with low polymer concentration could be well drawn. The gelation was caused by liquid–liquid phase separation even if crystallization followed gelation in the late stage; this was evident from the formation of transparent gel, a relatively small enthalpy of gel formation and the existence of two types of crystal structures. From the SEM measurements of dried gel films, spherulitic growth of crystals could be observed and the spherulites were bound by the crystalline ties.

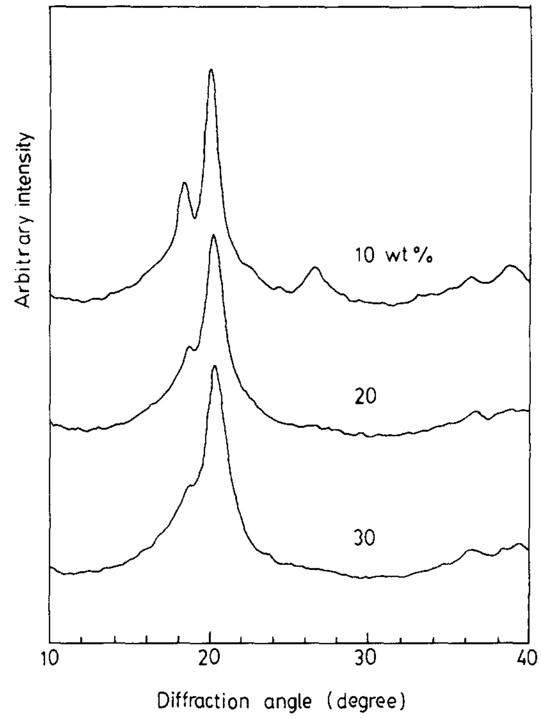

**Figure 8** X-ray diffractograms of dried gels with various PVDF concentrations

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