

Crystallization and Gelation of Poly(vinylidene fluoride) in Organic Solvents

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ABSTRACT: Poly(vinylidene fluoride) (PVdF) converts easily to thermally reversible gel at room temperature in aliphatic ketones or cyclic ketones such as 3-pentanone, 3-hexanone, cyclohexanone, and γ -butyrolactone, etc. Gelation of PVdF in these ketones took place through crystallization of polymers from solution. The crystallization process was investigated in detail by Fourier transform infrared (FTIR) measurements. The FTIR spectra were recorded continuously at room temperature until the solution converted to gel. It was suggested from spectral data that polymer chains packed together (i.e., crystallization took place) into the TTTGTTTG conformation in the case of PVdF/ γ -butyrolactone solution, followed immediately by gelation. On the other hand, crystallization occurred into the TGTG conformation in the case of other ketones and gelation immediately took place. Melting temperatures T_m^g of PVdF gels thus prepared from these solvents were measured. T_m^g showed a solvent dependence. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1517–1524, 1997

INTRODUCTION

It is well known that poly(vinylidene fluoride) (PVdF) can crystallize mainly to the following three structures, depending on the crystallization conditions: Form I (β -type crystal with planar zig-zag conformation), Form II (α -type crystal with the TGTG conformation), and Form III (γ -type crystal with the TTTGTTTG conformation). Besides the Forms I, II, and III, two other crystal structures (α_p -type and ϵ -type) were observed recently. These crystal structures have been studied in detail by many investigators^{1–4} from X-ray diffraction measurements.

In our previous study,⁵ PVdF in organic solvents (such as acetone, ethyl methyl ketone, or ethyl acetate) was found to convert to a thermally reversible gel at room temperature. In that study, morphological study of the gel was carried out using transmission and scanning electron microscopy. Independent of our study, Cho and col-

leagues⁶ reported thermoreversible gelation of PVdF in γ -butyrolactone solution.

It was considered in our previous study that gelation took place through crystallization in the case of a highly crystalline PVdF sample. In this sense, crystallization is one of the necessary conditions for gelation of PVdF solution. There are, however, no reports regarding correlation between crystallization and gelation of PVdF solution.

The main purpose of this study was to examine crystallization and gelation of PVdF solution, observing its solution directly by Fourier transform infrared (FTIR) spectrometry. Furthermore, detailed characterizations of the PVdF gels were carried out by differential scanning calorimetry (DSC), X-ray diffraction, and microscopic observation.

EXPERIMENTAL

Materials

The sample used here is PVdF-1, which was supplied by Kureha Chemical Industry Co. Physical

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Table I Typical Physical Properties of PVdF Sample

Sample	$\bar{M}_w \times 10^{-4}$ ^a	T_m ^b (°C)	ΔH_m ^c (J/g)	X_c ^d (%)
PVdF-1	47	176.2	60.5	57.8

^a Weight-average molecular weight determined by intrinsic viscosity.

^b Melting temperature.

^c Heat of fusion.

^d Degree of crystallinity estimated from DSC measurement.

properties of the sample are listed in Table I. X-ray diffraction measurements showed that this sample (original sample) had the Form II crystal structure, as shown in Figure 1(a).

Degree of crystallinity (X_c) of the present sample (PVdF-1) was determined from its DSC curve [Fig. 1(b)] using the following equation:

$$X_c = [\Delta H_m^s / \Delta H_m^*] \times 100(\%) \quad (1)$$

where ΔH_m^s and ΔH_m^* are the heats of fusion of the present PVdF sample and of perfectly crystalline PVdF, respectively. In this study, a value of 104.7 Jg^{-1} was used for ΔH_m^* , which was reported by Rosenberg and associates.⁷

Weight-average molecular weight (\bar{M}_w) was estimated from viscosity measurements. The intrinsic viscosity $[\eta]$ was determined in dimethylacetamide (DMA) at 25°C and \bar{M}_w was calculated using the following equation⁸:

$$[\eta] = 2.01 \times 10^{-4} \bar{M}_w^{0.675} \quad (2)$$

Solvents for gelations are γ -butyrolactone, cyclohexanone, cycloheptanone, 3-pentanone, 3-hexanone, 3-heptanone, and 3-octanone. These solvents are reagent grade and were used without further purification.

Preparation Method of Gel

A known amount of sample was dissolved completely in a solvent at 180°C using a sealed glass tube of about 50 cm length and 1 cm diameter. Then the sample tube was immersed in a well-stirred water bath kept at 30°C for 12 h to prepare a gel.

Measurement of Gel-melting Temperature

Gel-melting temperature (T_m^g) was measured by the so-called falling-ball method, which was pio-

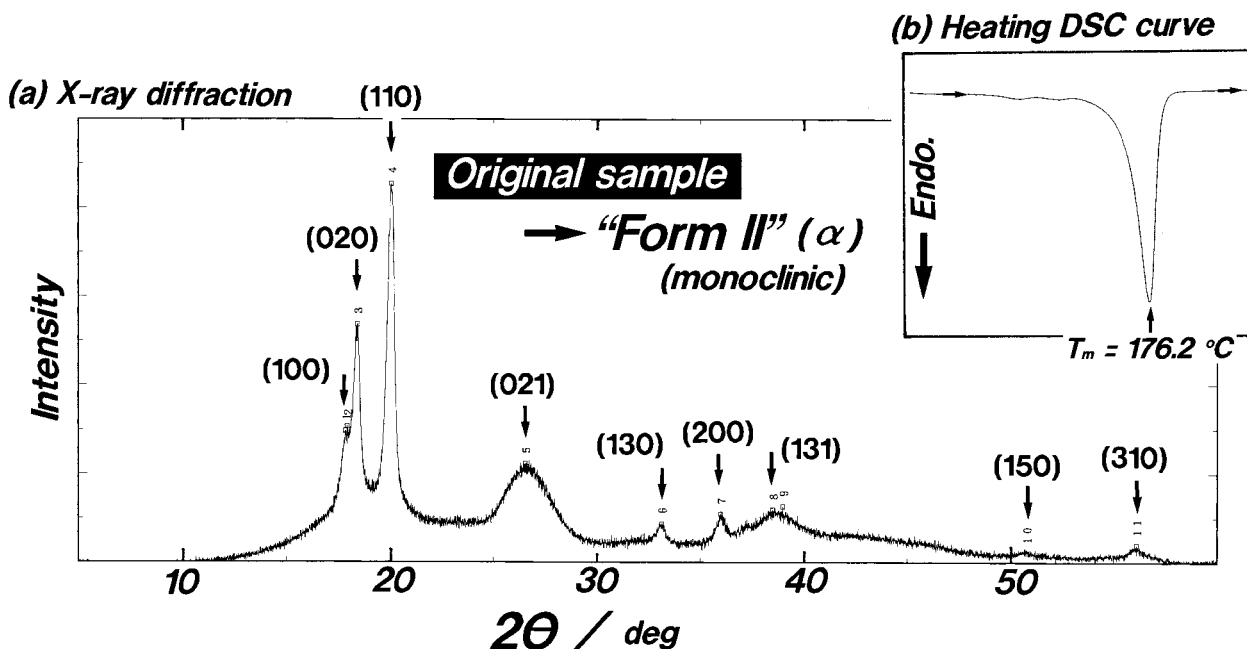


Figure 1 X-ray diffraction pattern (a) and heating DSC curve (b) of PVdF sample (PVdF-1).

neered by Takahashi and coworkers,⁹ using a steel ball of about 30 mg weight and 2 mm diameter. In case of 30-mg-weight ball, it did not influence T_m^g .¹⁰ A gel in a glass tube was heated from 30°C at a rate of about 0.3°C/min.

X-ray Diffraction Measurement

X-ray diffraction measurements were carried out using a Rigaku X-ray diffractometer, Model RINT-2500 VHF, with an experimental condition of 50 kV and 200 mA.

Lyophilized gels were used as specimens for X-ray measurements. Diffraction patterns were recorded using Cu-K α radiation with wavelength $\lambda = 0.15405$ nm.

FTIR Measurement

Infrared spectra were recorded using a JEOL Fourier transform infrared spectrometer, Model JIR-3505. One hundred scans at a resolution of 4 cm⁻¹ were averaged to obtain each spectrum.

The PVdF sample was completely dissolved in a solvent at about 180°C for 2 h in a glycerin bath. After the solution was maintained at room temperature for 10 min, it was poured into a KRS-5 cell (CIC Photonics Inc.; horizontal stand type; capacity: ca. 3 cm³). The polymer chains in the cell soon crystallized from the solution at room temperature. The FTIR spectra resulting from the crystallization process were recorded by the ATR method at intervals of 10 min.

Scanning Electron Microscopy (SEM)

Observation of crystallites formed in gel was carried out using a JEOL scanning electron microscope, Model JSM-T20. Specimens for SEM measurements were prepared as follows: After a gel was lyophilized, it was coated with a thin layer of gold by the vacuum evaporation technique.

Differential Scanning Calorimetry

DSC measurements were carried out with a Shimadzu heat flux differential scanning calorimeter, Model DSC-50, equipped with a thermal analysis data system for baseline correction, transition temperature, and calculation of the transition heat. All experiments were carried out at a heating rate of 10°C/min using a 10 mg sample under a constant flow of nitrogen gas.

RESULTS AND DISCUSSION

Gel-melting Temperatures

PVdF solutions converted to gels on cooling, which in turn converted to sols on heating. These sol-gel transitions were thermoreversible. Gelation of PVdF depended on the kinds of solvents; that is, gelation took place slowly at room temperature in γ -butyrolactone or cyclohexanone, whereas it occurred very quickly in aliphatic ketones such as 3-heptanone or 3-octanone. On the other hand, gelation did not occur in the solvents such as DMA, dimethylformamide (DMF), or dimethyl sulfoxide (DMSO). In a dilute solution below ca. 1 g/100 cm³, all systems did not convert to gels but crystalline precipitates were separated from solution; that is, crystal-liquid phase separation took place macroscopically.

When a hot PVdF solution (180°C) in a glass tube was immersed quickly in a water bath kept at 30°C, a turbid gel was formed, as shown in Figure 2(b). This turbid gel included many spherulites. On the other hand, as shown in Figure 2(a), almost-clear gel was prepared when the hot solution was cooled slowly from 180°C to 30°C at a cooling rate of ca. 0.1°C/min. In the slowly cooled gel, spherulites were not observed. Thus the morphology of PVdF gel is influenced strongly by the gel preparation method, particularly by the cooling rate of the hot solution. In this article, the focus is mainly on the rapidly cooled gel (i.e., a quenched gel).

The relation between T_m^g and polymer concentration (C) is shown in Figure 3. For any gelation solvent, T_m^g rises gradually with increasing polymer concentration. As a whole, T_m^g s are classified broadly into two groups by the gelation solvents. One is the group of gels prepared from aliphatic ketones (i.e., 3-pentanone, 3-hexanone, 3-heptanone, and 3-octanone). Gel-melting temperatures of this group are higher. The other group is gels prepared from cyclic ketones, such as cyclohexanone or cycloheptanone. In each group, a curve of T_m^g becomes higher with increasing number of carbon atoms of gelation solvent.

Takahashi and coworkers¹¹ derived the following equation for T_m^g s of crystalline polymer, assuming the junction points of gel to be crystallites comprised of ζ units in length and ρ crystalline sequences in cross section:

$$1/T_m^g = A - B \ln(V_2N) \quad (3)$$

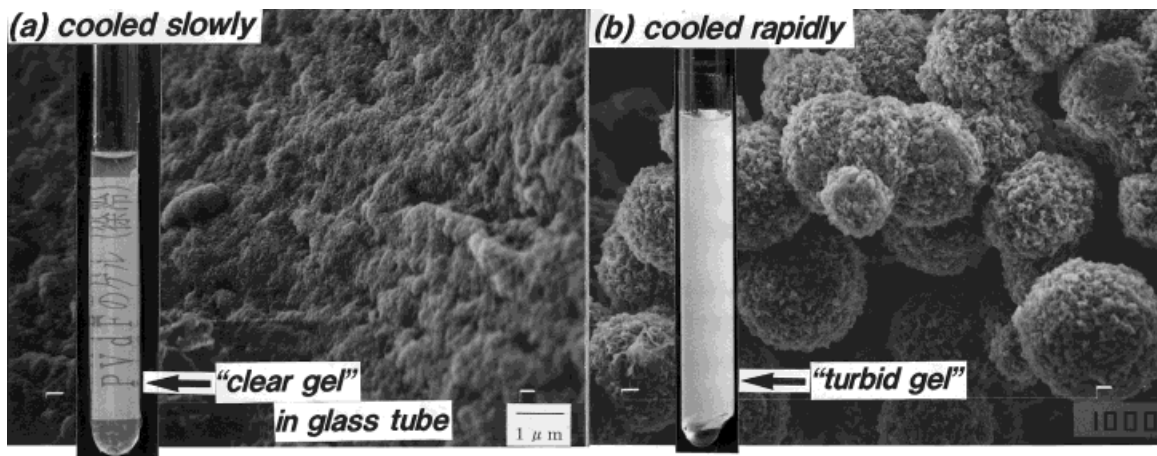


Figure 2 Comparison of two morphologies (a, b), of lyophilized gels. Both are PVdF-1/3-pentanone systems with the same concentrations: 10 g/100 cm³. In (a), the word "PVdF" behind the glass tube can be read through the gel and thus the clear gel is prepared.

where A and B are constants containing thermodynamic parameters and junction size ζ , V_2 is the volume fraction of the polymer, and N is the weight-average degree of polymerization.

According to eq. (3), it is expected that a plot of $1/T_m^g$ versus $\ln(V_2N)$ yields a straight line for each gelation solvent. The plots obtained for all

gelation solvents are illustrated in Figure 4. As expected, an excellent straight line was obtained for each gelation solvent. Taking account of the linear relationship obtained between $1/T_m^g$ and $\ln(V_2N)$ as shown in Figure 4, it is considered that junction points of PVdF gel are made up of crystallites.

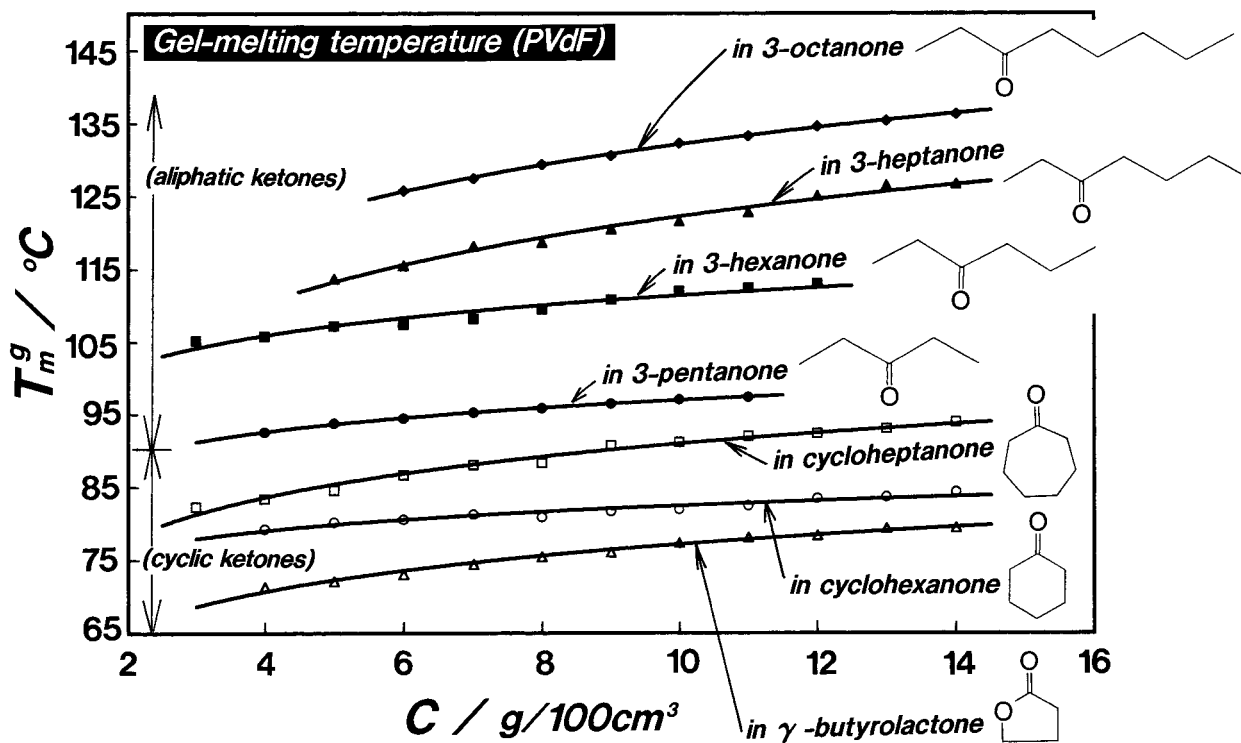


Figure 3 Relation between T_m^g and polymer concentration (C). One sample (PVdF-1) and seven kinds of gelation solvents are used.

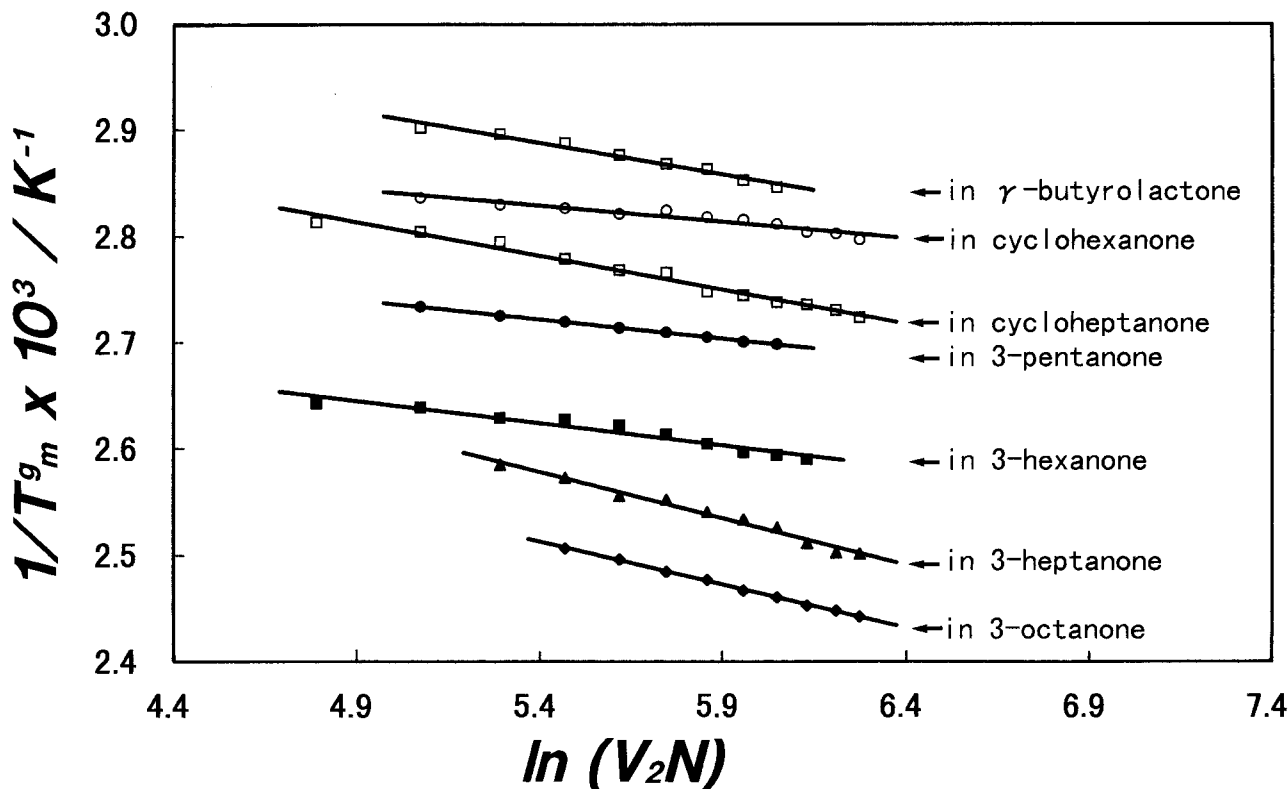


Figure 4 Plots of $1/T_m^g$ versus $\ln(V_2N)$ according to eq. (3).

FTIR Spectra

When a PVdF solution in an FTIR cell was maintained at room temperature, polymers were eventually crystallized from the solution and soon converted to gel. This crystallization process was recorded by FTIR. The FTIR spectra obtained for three systems, i.e., PVdF in (a) DMA, (b) γ -butyrolactone, and (c) cyclohexanone, are shown in Figure 5. The "time" shown in the left-hand side of each spectrum is the time measured after a PVdF solution was poured into the FTIR cell. In systems (b) and (c), gelation took place. In system (a), however, gelation did not occur. An absorption band associated with the appearance of TGT \bar{G} conformation (i.e., crystallization) was observed on the FTIR spectra. However, an absorption band associated with gelation (i.e., sol-gel transition) was not observed in the FTIR spectra. So, in order to investigate the correlation between crystallization and gelation of PVdF solution, the judgment whether PVdF solution was converted to gel or not was carried out by the test-tube tilting method.

It is well known that the region 400–600 cm^{-1} is sensitive to the PVdF conformation.¹² It is characteristic in Figure 5(b) that the absorption

bands at 511 cm^{-1} and 484 cm^{-1} become larger with increasing time. On the other hand, in Figure 5(c), the absorption band at 532 cm^{-1} appears after ca. 30 min (though this absorption is not observed after 20 min) and this 532 cm^{-1} band becomes larger with increasing time. In Figure 5(a), however, any characteristic absorption band changing with time is not observed. In this system (PVdF/DMA), crystallization and gelation did not occur.

Benedetti and coworkers¹² studied FTIR spectra of PVdF films, which were obtained by casting solutions in ethyl methyl ketone. According to their report, the absorption band at 532 cm^{-1} is characteristic of the conformation TGT \bar{G} (i.e., Form II). On the other hand, the lack of bands at 532 cm^{-1} and 471 cm^{-1} , and further, the presence of absorptions at 511 cm^{-1} and 484 cm^{-1} , generally indicate the presence of Form III.

Taking into account the study of Benedetti and associates,¹² gelation of the present system PVdF/ γ -butyrolactone solution [Fig. 5(b)] may occur taking the conformation TTTGTTT \bar{G} from random coil chains in solution, i.e., through crystallization of Form III. On the other hand, gelation of the system PVdF/cyclohexanone solution [Fig.

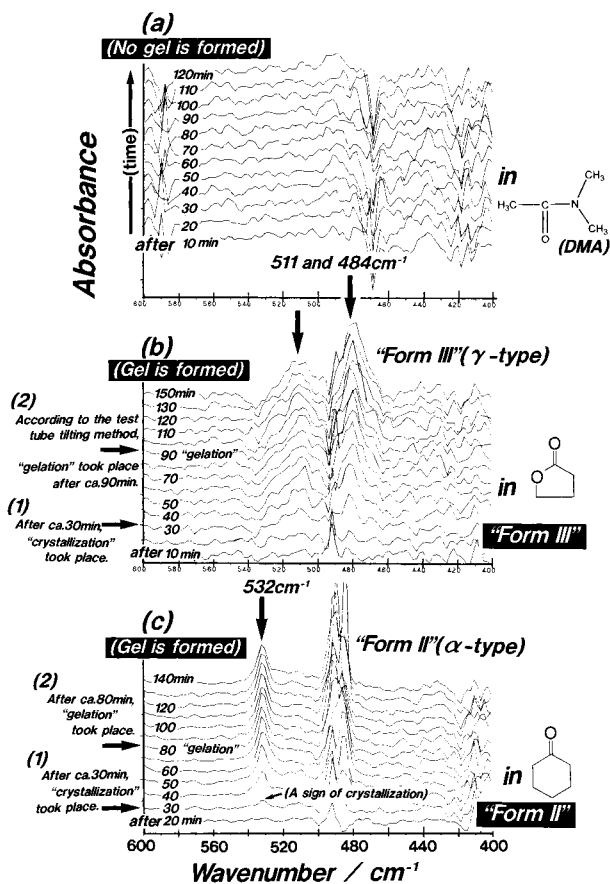


Figure 5 Relation between absorbance and wave number obtained for three systems with the same concentrations: 4 g/100 cm³. PVdF-1 (a) in DMA solution; (b) in γ -butyrolactone solution; and (c) in cyclohexanone solution. These FTIR spectra were recorded by the ATR method.

5(c)] may occur taking the conformation TGT \bar{G} , i.e., through crystallization of Form II. For other gelation solvents (such as cycloheptanone, 3-pentanone, 3-hexanone, 3-heptanone, and 3-octanone), the same FTIR spectra as Figure 5(c) were obtained, and thus the gelation in these solvents is considered to occur through crystallization of Form II. The structures of crystallites formed in gels were investigated in more detail by X-ray diffraction.

X-ray Diffractions

X-ray diffraction patterns are shown in Figure 6, where (a) is the diffraction pattern obtained for lyophilized gel of PVdF/ γ -butyrolactone system [see morphology (d)] and (b) is the diffraction pattern obtained for lyophilized gel of PVdF/cyclohexanone system [see morphology (e)]. As

shown in Figure 6(b), lyophilized gel showed large diffraction peaks near $2\theta = 18.4^\circ$, 20.0° , and 26.6° . It is well known that these diffraction peaks are characteristic of the Form II crystal structure.³ On the other hand, in Figure 6(a), the diffraction peaks at $2\theta = 18.5^\circ$ and 20.1° are observed, and these peaks are characteristic of the Form III crystal structure.³ Accordingly, it was found from X-ray diffractions that the system PVdF/ γ -butyrolactone [see Fig. 5(b)] gave the crystal structure of Form III, i.e., γ -type crystal with TTTGTTT \bar{G} conformation; whereas the system PVdF/cyclohexanone [see Fig. 5(c)] gave the crystal structure of Form II, i.e., α -type crystal with TGT \bar{G} conformation.

It is well known that thermoreversible gel is formed from solution as a consequence of the formation of a three-dimensional network whose junction points consist of physical bonding.¹³ Therefore, various types of three-dimensional networks of gels are formed from solutions depending on the mode and magnitude of molecular interaction between polymer and solvent. For example, the following three types of networks are observed^{14–16}: (1) a network whose junction points are crystallites; (2) a two-phase system accompanied by liquid–liquid phase separation (or spinodal decomposition); and (3) a network by molecular association, such as a hydrogen-bonding interaction. The type (2) network is usually formed in the polymer-rich phase.

In the systems studied here, gelations occurred through crystallization and thus junction points of gel network are considered to be made up of crystallites. According to the results in Figure 5(b,c), it may be possible to suppose that random coil chains in a PVdF solution gather together to take the specific conformation with increasing time, e.g., TGT \bar{G} conformation in the case of cyclohexanone solution and TTTGTTT \bar{G} conformation in the case of γ -butyrolactone solution.

In addition, difference in T_m^g measured in different solvents should be noticed (see Fig. 3). This indicates the presence of a solvent effect on the PVdF gel. Recently, solvent effect on the physical gelation in cooling polymer solution has been critically reviewed by Guenet.¹⁷ In PVdF/organic solvent systems studied here, there probably is a process in which solvent molecules with functional groups are placed at specific positions near PVdF chains by specific interaction (e.g., hydrogen-bonding interaction) between polymer and solvent. Differences in interaction intensities between polymer and solvent may cause the different kinds of conformation forms. Crystallization

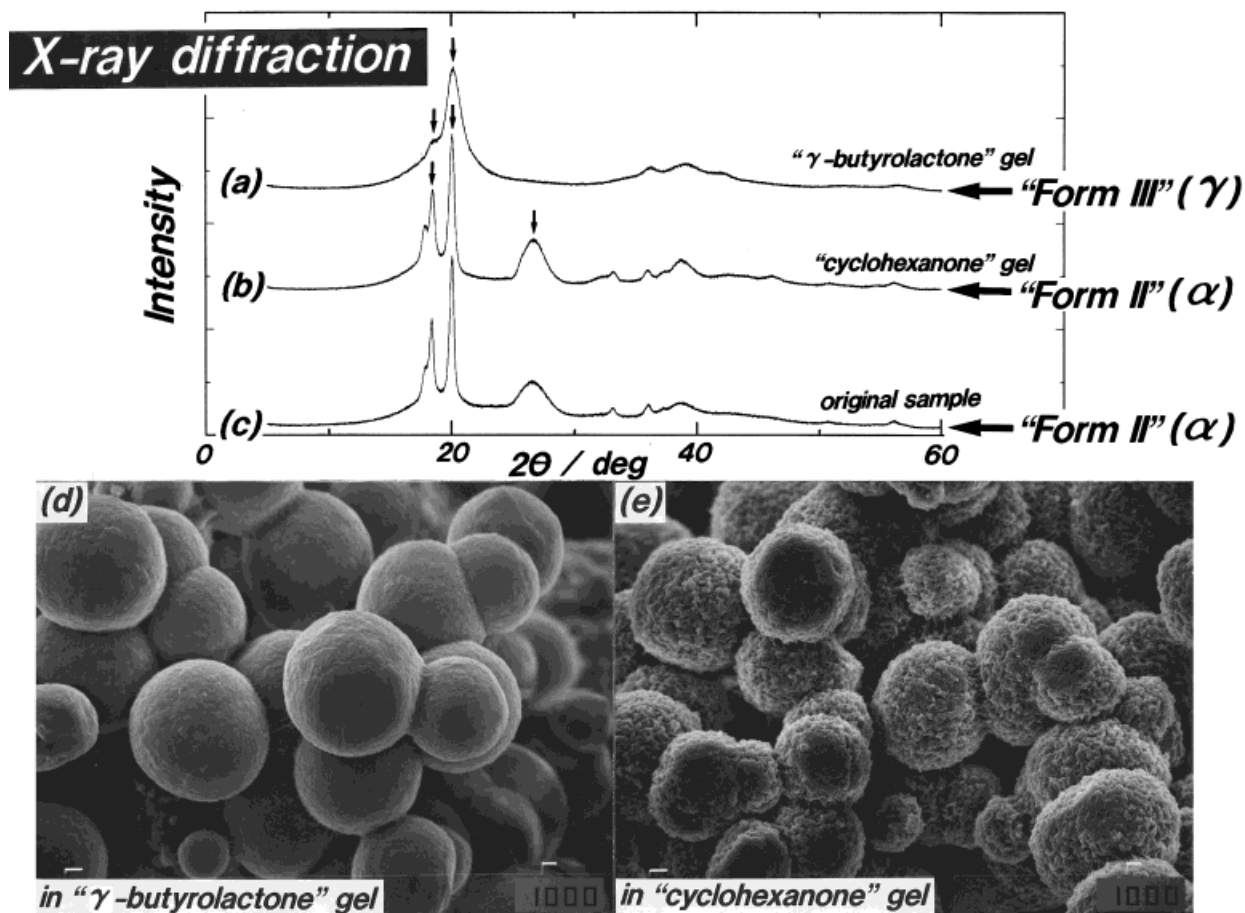


Figure 6 X-ray diffraction patterns [(a–c)] and morphologies [(d, e)] of lyophilized gels with the same concentrations: 20 g/100 cm³.

then occurs taking the specific conformation, finally leading to gelation. In fact, solvents containing >C=O group were dominant to form PVdF gel structure in this experiment. Interaction between >C=O group in poly(methyl methacrylate) (PMMA) and PVdF molecules in their blending has been already reported.¹⁸ Taking this report into account, it is strongly expected in this study that there are interactions between PVdF gel and the solvent.

According to the study of Cho and colleagues,⁶ gelation of the PVdF/ γ -butyrolactone system is caused by liquid–liquid phase separation in the early stage of gelation, and crystallization occurs in the late stage of gelation. At any rate, in order to discuss the detailed mechanism of gelation it is necessary to construct the phase diagram of PVdF in organic solvents. This problem is left for future study. For the present article, only quenched gels were studied. Slowly cooled PVdF gels will be reported in a subsequent article.

CONCLUSION

The present study clarifies the following results for the crystallization and gelation of PVdF solution:

1. PVdF in organic solvents (particularly in ketones such as 3-pentanone, 3-hexanone, cyclohexanone, and cycloheptanone, etc.) converts to a thermally reversible gel from a moderately concentrated solution.
2. Crystallization and gelation occur, taking the conformation of TTTGTTT \bar{G} in γ -butyrolactone solution and TGT \bar{G} in other ketones.
3. Gel-melting temperature increases slowly with increasing polymer concentration and obeys well the Takahashi theory, suggesting that junction points of PVdF gel are made up of crystallites.

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