Gelation and Crystallization of Poly(4-methyl-1-pentene) in Cyclohexane Solution

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ABSTRACT: Four crystal modifications of poly(4-methyl-1-pentene) were found in cyclohexane gels by means of X-ray diffraction. The gel phase was divided into several regions by the observation of these modifications. The gels in different regions had different morphologies, which were observed by means of optical microscopy. These varieties revealed mainly two kinds of gels according to whether the gelation was caused by liquid–liquid phase separation or by solid–liquid separation (crystallization). In the gel regions where extraordinarily big spherulites and white particles were precipitated from the homogeneous solution, the mechanism of the solid–liquid phase separation could be visually detected. In this case gelation means the formation of a linked structure by nucleation and growth of the crystallites from the homogeneous solution. On the other hand, the regelation from the ordinary 0 °C gel was a good example of liquid–liquid phase separation. The mechanism was evidenced by the following facts: the presence of transparent and semitransparent gels, the double structure of the X-ray diffraction pattern, the two-step change of the transparency of the gel on heating, and the characteristic morphology. In this case the gel was formed by a certain molecular overlapping in the polymer-rich phase besides the crystallization.

Introduction

Recently, a noncrystallizable polymer, atactic polystyrene, was found to exhibit thermoreversible gelation with certain solvents.[1,2] It is very interesting that the sol–gel transition could be described in terms of phase separation, showing that crystallization is not a necessary condition for gelation. This rule would hold true also in the case of crystalline polymers. However, crystallization necessarily occurs in the finally produced gel of crystalline polymers, even if gelation occurs without crystallization. Whenever crystallization occurs in solution before gelation or in the gel phase after gelation, the crystal structure of the finally produced gel is a useful clue to the mechanism of gelation.

Among various orders of structure, we used the crystal structure, which was detected by wide-angle X-ray diffraction because of its convenience. Further, if in a crystalline polymer/solvent system various crystal modifications appear depending on its gelation condition, the system is especially useful for our purpose. Unfortunately, only one crystal modification exists in the case of poly(vinyl alcohol), which has been investigated in our laboratory,[3–7] and also for other polymers. However, Keller et al. have found in a drawn gel of the isotactic polystyrene (iPS)/decalin system two crystal modifications that have different molecular orientations to each other: a normal 3/1-helical conformation and an abnormal extended one.[8–11] For the drawn gel, they proposed a structural model in which the chain-folded crystals composed of the former lie in fringed-micellar junctions composed of the latter (double structure). To our knowledge, this is the first case where polymorphism has been used for structural investigation of gels. They also applied this model to a poly(vinyl chloride) (PVC) gel.[12–15]

Recently, Delmas et al. reported that isotactic poly(4-methyl-1-pentene) (P4M1P) has five different modifications when crystallized from solutions and gels with various solvents.[16,17] P4M1P is more crystallizable and has more crystalline forms than iPS. These facts provided a reason for selecting P4M1P for the investigation of the gelation mechanism of crystalline polymers. We expected that the various crystal modifications could be formed by more complete control of the gelation conditions, such as polymer concentration and temperature, even if P4M1P was gelled in only one solvent.

Experimental Section

Polymer and Solvent. A commercial isotactic P4M1P sample (TPX, MX019, Mitsui Petrochemical Co., Ltd. Japan) supplied as pellets was used throughout this work. In the light of recent work by Aharoni et al. on the gelation of P4M1P,[16] we chose cyclohexane as the solvent because two crystal modifications (forms II and IV) were found in its interaction with P4M1P. Cyclohexane is characterized also by its high freezing point (6.5 °C) and its high volatility.

Preparation of Solutions. Solutions were prepared by dissolving the polymer at 130 °C in 2.5 mL of solvent at the desired concentrations (c = (g of polymer)/(mL of solvent)) in sealed test tubes of 12-mm diameter and 110-mm length. The tube was sealed after freezing the cyclohexane in dry ice–methanol to prevent its vaporizing. The first dissolution was performed by repeatedly turning the tube upside down over about 24 h.

Preparation of Gels. The gels were prepared by the two methods shown in Figure 1. One is "ordinary gelation"; the original solution was quenched from 130 °C to a given gelation temperature (T_{gel}) and stored for a given time. The other method is called "regelation"; the ordinary gel was formed at 0 °C, which was termed "0 °C gel", was melted to a sol by temperature jumping to 90 °C, and then was allowed to form a gel at the regelation temperature (T_{gel}'). These methods are not independent of each other. The latter method was originally employed to confirm the characteristic regelation behavior during heating of the ordinary 0 °C gel, as will be mentioned later. The dissolution temperature of 90 °C in the regelation procedure was selected as the lowest common melting temperature in the temperature jumping of the ordinary 0 °C gels. Without the ordinary 0 °C gelation process or with the increase above 5 °C of the temperature of its process in the regelation, the characteristic regenerated gel could not be formed. A "20 °C storing and drying" process was set up by both methods to yield dried samples for X-ray diffraction and optical microscopy.

The gel is defined as the state where no flow occurs in an inverted test tube. The concentration below which no gelation occurs, termed the critical gel concentration (CGC), is determined at each gelation temperature, ranging from 0 to 90 °C. The gel sample was repeatedly dissolved at 130 °C over about 4 h and was successively used for the next gelation cycle. In the case where the gelation temperature was below the freezing point of the solvent, the sample did not flow whether it was gel or sol. Thus the sample was stored at 10 °C for 30 min to melt the solvent and determine the CGC. No additional gelation and crystallization were observed in this melting process.

Observation of Crystallization. Crystallization in solution and in the gel was detected as a whitening with the naked eye. In the particular case that extraordinarily big spherulites were precipitated, their nucleation, growth, and impingement were

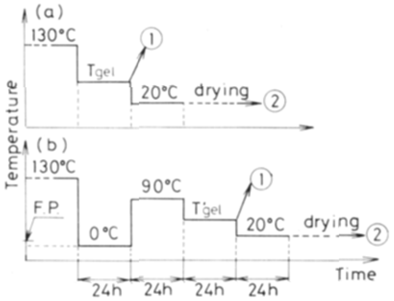


Figure 1. Two methods for preparation of gels are shown by temperature profiles: (a) ordinary gelation and (b) regelation. The arrows labeled 1 represent a heating process for the measurement of the melting temperature of the gel. The arrows labeled 2 represent a process of storage at 20 °C and subsequent drying for X-ray diffraction and optical microscopy.

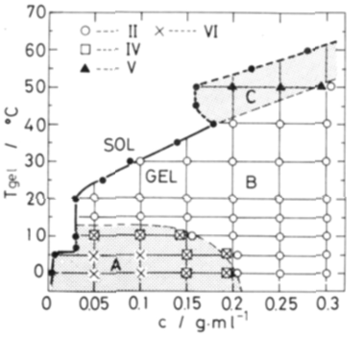


Figure 2. Gelation temperature vs. polymer concentration phase diagram of the P4M1P/cyclohexane system prepared by the ordinary method: (●) CGC curve, (--) the lowest gelation concentration after storage for 24 h. Several symbols marked on a lattice express crystal forms of dried gels.

easily observed without any device because they were semitransparent in the early stage of crystallization.

Melting Temperature of Gel. The apparent melting temperature of the gel was determined by Eldridge and Ferry's method.[18] The gel sample was placed upside down in a well-stirred poly(ethylene glycol) bath at T_{gel}, and the bath was warmed at the rate of about 0.2 °C/min, as the arrows labeled 1 in Figure 1 show. The temperature at which the gel fell to the bottom of the test tube was taken to be the gel melting temperature (T_m).

X-ray Diffraction Photographs. Dried gels were used for taking X-ray diffraction photographs. The gel was stored at 20 °C for 24 h after gelation, dried for 1 week, and further dried under vacuum for 24 h, as the arrows labeled 2 in Figure 1 show. The dried gel was gently condensed if it was a powder or was sliced if it was resinous to form a disk of about 0.5-mm thickness. No crystal transformation was observed during these sample reformings.

X-ray diffraction photographs were taken with a flat-plate camera equipped with a pinhole collimator of 1.0-mm diameter. Nickel-filtered Cu Kα radiation was provided by a Rigaku-Denki Geigerflex under 40 kV and 20 mA. The irradiation time was 10 min. The distance from specimen to film was 5 cm. The crystal form was identified only by the X-ray diffraction pattern.

Optical Microscopy. The gel, which was stored at 20 °C for 24 h after gelation, was taken from the sealed tube and immediately fractured in order to observe the inner surface of the gel. Transmission optical microscopic observation was conducted with a Nikon microscope. In spite of not having been dried, the observed gel was in the same state as the dried gel used for the X-ray diffraction because of the high volatility of the solvent and the thinness of the sample.

Results

1. Ordinary Gelation. 1.1. Classification of the Gel by Crystal Modifications.

The CGC curve shown in Figure 2 is for gelation after storing for 24 h. The gel phase was divided into three regions (A, B, and C) by means of the crystal modifications. Observations of the visual form and color of the dried gels were also useful to determine the boundary lines of the phase diagram; in region B white powder samples appeared, whereas almost transparent and resinous samples were obtained in regions A and C, which sandwich region B. The X-ray diffraction photographs of these modifications are shown in Figure 3. The nomenclature used is that of Delmas et al.,[17] except form VI, which is added by us. Before them, Takayanagi et al. had found three of the crystal modifications (I, II, and III) by crystallization from the dilute solution of xylene.[19,20] Takayanagi's modifications coincide with forms I, IV, and II in Figure 3, respectively. The most frequently observed form I has no direct relation to the gelation in this system. However, the dried gels were irreversibly transformed into form I on heating.

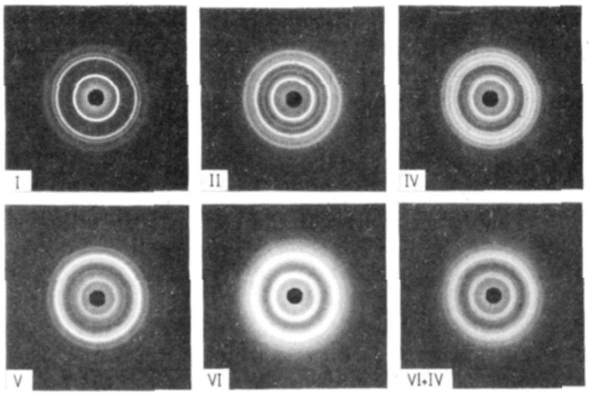


Figure 3. X-ray diffraction photographs of the dried gels. Except for forms I and IV, these gels were prepared by the ordinary method. Form I crystal was obtained by heat-treatment of the other dried gels at a certain temperature. Form IV crystal was prepared by the regelation method.

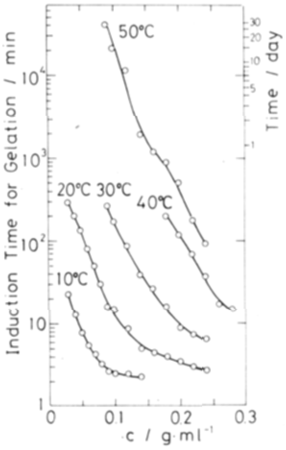


Figure 4. Induction time for the ordinary gelation at various T_{gel} as a function of polymer concentration. Temperatures shown in the figure are the gelation temperatures (T_{gel}).

1.2. Induction Time for Gelation. In Figure 4 the induction time for the gelation is plotted as a function of the concentration. The induction time in region C (50 °C) was much higher than that in the other regions. For 50 °C gelation the lowest concentration, below which any gelation could not be observed after 24 h storing, was not taken as an equilibrium CGC but as a reference value because the gelation (crystallization) had not been terminated at low concentrations, even after storing for 30 days.

The rates of gelation and polymer crystallization were larger than that of freezing of the pure solvent below the freezing point. They were too fast to measure exactly. Furthermore, no macroscopic change in the gel was ob-

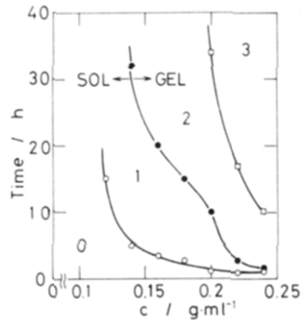
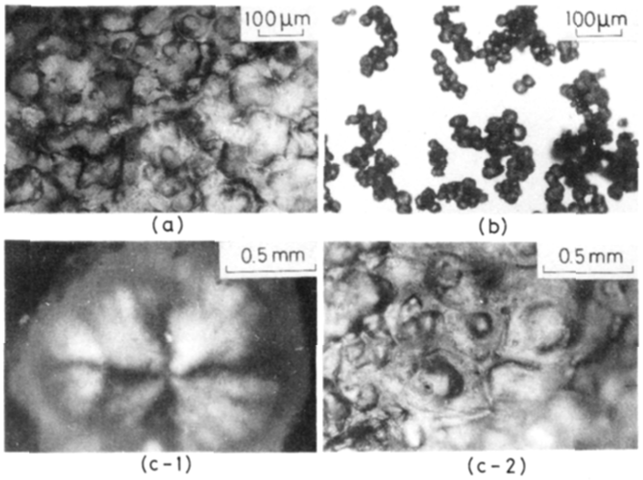


Figure 5. Times for onsets of nucleation (○), gelation (●), and end of crystallization (□), when the solution was quenched and stored at 50 °C.



(a) (b)

(c-1) (c-2)

Figure 6. Optical microscopic photographs of the dried gels prepared by ordinary gelation: (a) Fracture surface of a gel in region A ($c = 0.1$ g/mL, $T_{gel} = 0$ °C); (b) powder of a gel in region B (0.05 g/mL, 20 °C); (c-1) spherulite crystallized from a solution near region C (0.15 g/mL, 50 °C); (c-2) sample surface of a dried gel in region C ($c = 0.25$ g/mL, 55 °C). (a), (b), and (c-2) are seen under unpolarized transmitted light, and (c-1) is viewed between crossed polars.

served during the induction time for pure-solvent freezing. In the sol phase, however, freezing could be observed, which made it difficult to determine the CGC.

1.3. Relation between Crystallization and Gelation. The relation between the rates of gelation and crystallization was very characteristic, depending on the gelation regions. In region A at the early stage of gelation the gel was transparent and soon became turbid due to crystallization. In region B white particles of crystallites precipitated homogeneously in the sample. When the whitening ceased, the gel was formed. In region C big spherulites of 0.5–2.0-mm diameter were nucleated and grew to impinge on each other, forming a semitransparent gel. In this region, the rate of crystallization was so moderate and the spherulites were so big that one could observe the gelation mechanism carefully with the naked eye, as Figure 5 shows.

1.4. Morphology. Optical micrographs of the dried samples are shown in Figure 6. In region A a nodule structure was observed, as Figure 6a shows. The grains of the structure units were completely intertwined with each other. In regions B and C, two types of crystallites were precipitated, as described in the previous section. Both seemed to be spherical and to have a narrow size distribution. In region B a number of particles aggregated where $c < 0.1$ g/mL, as Figure 6b shows, and stuck together where $c > 0.1$ g/mL. (The size was 20–30 μm in the former region and 5–8 μm in the latter.) These particles were not termed spherulites because no Maltese cross was observed under cross-polarized light. On the other hand, in region C big sperulites of 0.5–2.0-mm diameter, measured in the dried state, which showed Maltese crosses, were observed. They contacted each other in the gelation and became warped in drying, as Figure 6c-2 shows. However, a completely crystallized but nongelled spherulite could be picked up from the sol phase 1 (in Figure 5), as Figure 6c-1 shows, where it was cut in semicircular slices.

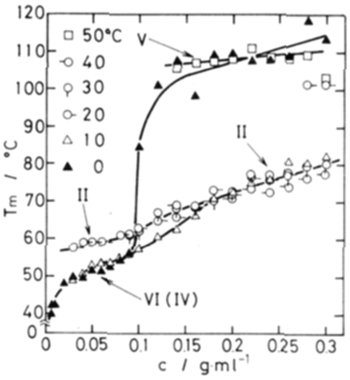


Figure 7. Dependence of melting temperature (T_m) on polymer concentration for ordinary gel prepared at various T_{gel}.

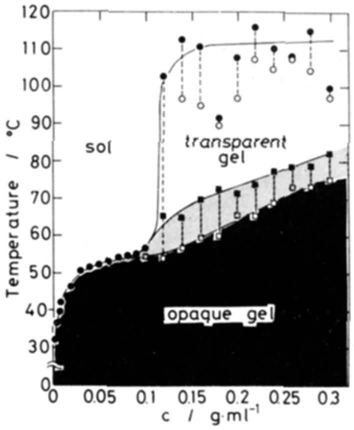


Figure 8. Phase change with increasing temperature for ordinary 0 °C gel: (●) gel melting temperature; (■) clearing temperature; (○, □) onsets of melting and clearing, respectively.

Above and below the freezing point no morphological difference was observed in regions A and B, respectively.

1.5. Melting. Figure 7 shows the gel melting temperature as a function of concentration. The melting occurred when the gel became transparent owing to dissolution of the crystallite. T_m clearly depends on the crystal forms. These rules could not be applied to 0 °C gels at $c > 0.1$ g/mL. Although they became transparent at the dissolution temperature, some of them remained at higher temperatures, retaining the gel state, as Figure 8 shows. However, melting occurred with some irregularity and at long intervals compared with the other gels. Furthermore, the 0 °C gels simultaneously fell to the bottom under fast temperature jumping to 90 °C. These facts indicate that the heating rate was so slow that some of them could be regenerated into new gels with higher melting temperatures.

The relationship between T_m and c was proposed by Eldridge and Ferry.[18]

$$\ln c = \text{const} - \Delta H_m / RT_m \tag{1}$$

where ΔH_m is the apparent enthalpy change of the gel melting and R the gas constant. It was originally derived for a network formed by physical associations between two

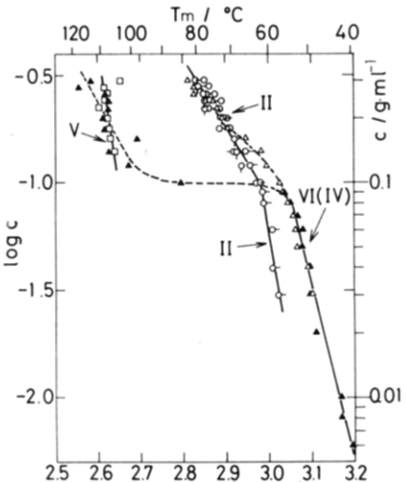


Figure 9. Plots of $1/T_m$ vs. log c for ordinary gels prepared at various T_{gel}. The symbols are the same as in Figure 7.

Table I
Enthalpy Change of Gel Melting (ΔH_m) for Ordinary Gels

	ΔH_m/kJ·mol^{-1}	
T_{gel}/°C	c < 0.1 g·mL^{-1}	c > 0.1 g·mL^{-1}
0	159 (VI)	(48)
10	136 (VI, IV)	40 (II)
20	266 (II)	57 (II)
30		59 (II)
40		55 (II)
50		144 (V)

chains. Nevertheless, we applied it also to the gel formed by the aggregation of the crystallites in regions B and C. In such crystallizable gels the temperature of gel formation is usually used rather than T_m. Thus, our derived values of ΔH_m are apparent values but would be useful to discuss properties and structure of the gel within our system. The data in Figure 7 were transformed to a ln c vs. $1/T_m$ plot to affirm the linear relationship of eq 1 for each crystal form (Figure 9). The values of ΔH_m by the use of eq 1 are listed in Table I. The gels with the same form II have two kinds of ΔH_m values above and below c = 0.1 g/mL. This is probably due to the size difference of the particles between them, as described in section 1.4.

2. Regelation. 2.1. Induction Time for Gelation. The CGC curve of the regelation is shown in Figure 10. In this figure, the lowest concentration of the regelation at a given induction time is also shown as a function of T_{gel}'. No distinction with ordinary gelation could be observed in the narrow region around the point (c = 0.05 g/mL and T_{gel}' = 20 °C) hatched in Figure 11. Thus, we will discuss the regelation except in this region. In the other region the induction time becomes 1 or 3 orders of magnitude smaller than that of ordinary gelation. For the transformation of the ordinary 0 °C gels to new gels at c > 0.1 g/mL without failing during the heating, three conditions are necessary: (1) the crystallites dissolve over a temperature range in which the regelation can occur; (2) the dissolution occurs over a wide temperature interval; (3) the regelation rate is large compared with the heating rate. Interestingly, the range of the transformation during the heating lies parallel to the two lowest concentration curves of 2-min and 10-min induction times, as the hatched dissolution region in Figure 10 shows. Similar regelation was observed for a gel of a syndiotactic-rich poly(vinyl alcohol)/water system.[7]

2.2. Classification of the Gel by Crystal Modifications. As Figure 11 shows, the regenerated gel phase was divided into three regions (A′, D, and E). It is not easy to distinguish region E from region D in accounting only for the crystal form of the dried gel. As described in a later section, form IV composed in the regenerated gel in region E was additionally formed in the last preparation stage of storage at 20 °C.

2.3. Crystallization in the Regenerated Gel Phase. The regenerated gel was transparent at the early stage of gelation. The whitening due to crystallization proceeded to a limit in regions A′ and D. On the other hand, it did not reach its limit at T_{gel}' in region E. Moreover, an entirely transparent gel existed stably at the lower concentration region at T_{gel}'. However, it was also completely crystallized in the next storage at 20 °C. The difference between regions E and D was most successfully revealed by taking the case of T_{gel}' = 40 °C as an example. Figure 12 shows the time required for the gelation and the crystallization. After storage at 24 h four kinds of phase appeared: transparent sol, uncrystallized transparent gel, partly crystallized semitransparent gel, and completely crystallized opaque gel. "Partly crystallized" gel left, homogeneously in the gel phase, the domain in which further crystallization could be induced by quenching to a lower temperature. The boundary concentrations that divide these phases are shown at the upper part of this figure. They did not shift even after storing for 1 week. Although region E consisted of two phases, we will not divide it to avoid further complication. The X-ray diffraction pho-

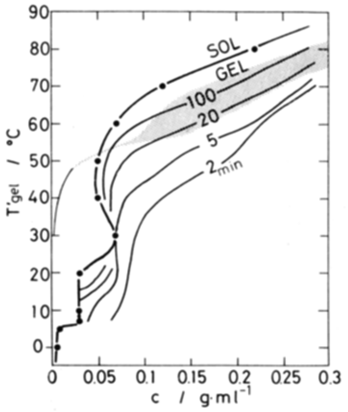


Figure 10. CGC curve for the regelation (●). The four solid lines shown in the region of the gel phase represent change of the lowest gelation concentration with storing time. The hatched region corresponds to that for crystal dissolution of the ordinary 0 °C gel (see Figure 8).

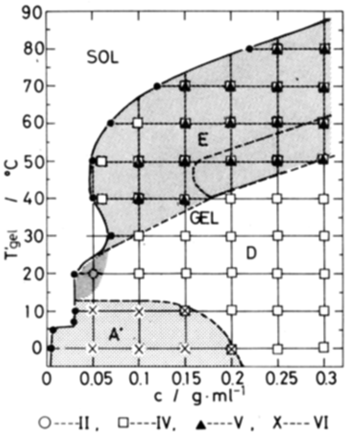


Figure 11. Regelation temperature vs. polymer concentration phase diagram of the P4M1P/cyclohexane system, where the gels were formed by the regelation method. Several symbols marked on a lattice express crystal forms of dried gels.

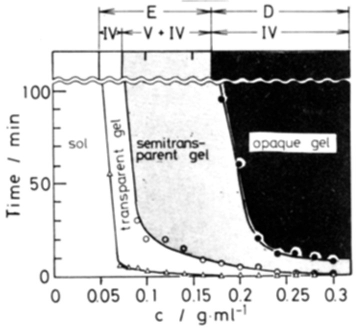
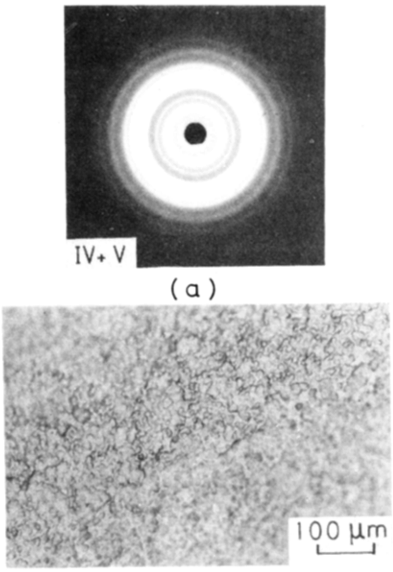


Figure 12. Times for onsets of gelation (△) and crystallization (○) and for end of crystallization (●), for the regelation at T_{gel}' = 40 °C.



(a)

(b)

Figure 13. X-ray diffraction (a) and optical microscopic (b) photographs for a regenerated gel formed in region E (c = 0.15 g/mL, T_{gel}' = 50 °C). The latter is seen under unpolarized transmitted light.

tograph of a dried gel from region E showed the double structure (forms IV and V) as Figure 13a shows. It is suggested that the crystallized domain of the gel in region E consisted of form V at T_{gel}' and the uncrystallized domain was occupied by form IV in storage at 20 °C. It was supported by the fact that the content of form IV was proportional to the transparency of the gel at T_{gel}'.

2.4. Morphology. As Figure 13b shows, a peculiar morphology was observed in the wholly regenerated gels. This morphology and the manner of the gelation and crystallization were similar to those in region A. Crystallites such as particles or spherulites were not found in the regenerated gel.

2.5. Melting. Figure 14 shows the dissolution temperature of the crystal and the gel melting temperature of the gel crystallized in two steps as shown at the upper part of this figure. The dissolution occurred also in two steps in the gel phase; the first clearing at about 57 °C was due to the dissolution of form IV and the second one was that of form V. It was evidenced that the crystallization and dissolution of form IV thermoreversibly occurred in the gel phase. It was interesting that the regenerated gels of $c < 0.1$ g/mL were stable at high temperatures in spite of their transparency.

The regenerated gels formed above 40 °C exhibited a high melting temperature ($T_m > 90$ °C). On the other hand, the gels formed below 30 °C showed irregular melting similar to that of the ordinary 0 °C gel. As Figure 15 shows, ΔH_m values of these gels were obtained by applying the Eldridge et al. plot to the regions of high melting temperature. The regenerated 50 °C gel was the most stable one.

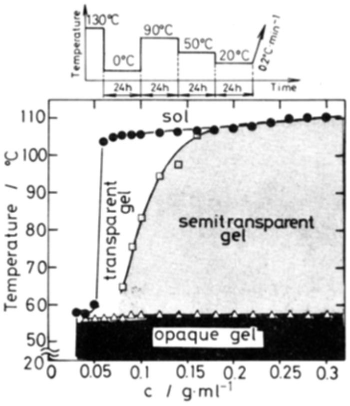


Figure 14. Phase change with increasing temperature for regenerated gels prepared according to a process shown in the upper part of this figure: (●) gel melting temperature; (△) temperature of first clearing from opaque gel to semitransparent or transparent gels; (□) temperature of second clearing from semitransparent gel to transparent gel.

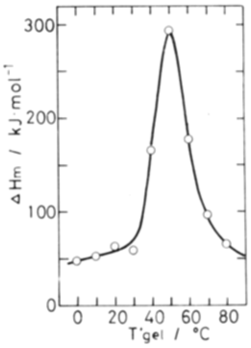


Figure 15. Enthalpy change of gel melting (ΔH_m) plotted against T_{gel}' for the regenerated gels.

Discussion

Two types of mechanisms were observed for gelation in this system. One is solid–liquid phase separation in regions B and C of the ordinary gelation. The other is liquid–liquid phase separation in region A of the ordinary gelation and the whole region of the regelation.

1. Gelation by Solid–Liquid Phase Separation. The mechanism is intrinsically the same as crystallization from homogeneous solution. Nuclei of crystallites grow freely until they aggregate to make a three-dimensionally linked structure that takes up the whole of the solvent. Thus, the formation of the linked structure means gelation. The secondary crystallization in the precipitated crystallites proceeded even after gelation. The aggregated structure is supported by the fact that melting of the gel is caused by dissolution of the crystallites. We will report on this gelation mechanism in detail in our next paper.

2. Gelation by Liquid–Liquid Phase Separation. Liquid–liquid phase separation takes place in the early stages of gelation. Gelation is caused by some overlapping of polymer chains in the polymer-rich phase without crystallization. Although some noncrystallized gels were stable, especially at lower concentrations in region E, the crystallization (solid–liquid phase separation) necessarily occurred within the two-phase gel at the final stage at room temperature. Crystallization is shown not to be the necessary condition for gelation even in the case of such a highly crystalline polymer.

There are five pieces of evidence showing that the gelation is caused by liquid–liquid phase separation:

(1) Gelation occurred in a transparent state (section 1.3 and Figure 12).

(2) Some semitransparent gels existed in an equilibrium state between transparent and opaque gel (Figure 12). This shows that crystallization proceeds in the polymer-rich phase.

(3) Two types of crystal forms appeared in one gel when some of the semitransparent gels were cooled to completely crystallize (two-step crystallization) (Figure 13a). The crystal form was different in the polymer-rich and polymer-poor phases.

(4) Some of the two-step crystallized gels showed two-step dissolution on heating (Figure 14). With increasing temperature, the crystallites in the polymer-poor phase dissolved at a lower temperature and then those in the polymer-rich phase dissolved.

(5) The optical morphology of the dried gels left a trace that is characteristic for liquid–liquid phase separation (Figures 6a and 13b). This is indirect evidence of the existence of the two phases that had formed at the early stage of gelation without crystallization.

From the above discussion, the boundary line between regions A and B means the binodal curve. Regelation extends the gel region to higher temperatures (Figures 10 and 11). Why can the gelation region be easily enlarged by regelation? It would be more reasonable that the particular molecular interaction formed between the solvent and polymer at 0 °C could live on even after melting at 90 °C and become the trigger that easily induces the liquid–liquid phase separation at the subsequent regelation stage. The interaction may be related to the freezing of the solvent because 0 °C is lower than the freezing point of the pure solvent.

We observed two kinds of gel structure. The structure for the liquid–liquid phase separation is very similar to that of Keller's model as regards the duplicity of the structure. The aggregated structure for the solid–liquid phase separation has not yet been found in the gels of poorly crystallizable polymers such as iPS and PVC. In the latter polymers the fringed micelle crystallite may be more acceptable rather than the lamella-like one. However, we could not observe in our gels positive evidence for the existence of the fringed micelle. If a phase diagram like that in Figure 2 was drawn also for the iPS system, more strict comparison would be made between the two polymers.

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Registry No. Isotactic P4M1P, 24979-98-4; cyclohexane, 110-82-7.

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Polarized Raman Spectra and LO–TO Splitting of Poly(vinylidene fluoride) Crystal Form I

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ABSTRACT: An LO–TO splitting ($\Delta\omega = \omega_{LO} - \omega_{TO}$) of Raman bands has been observed for poling-treated poly(vinylidene fluoride) (PVDF) crystal form I, where ω_{LO} and ω_{TO} are vibrational frequencies of longitudinal and transverse optical modes, respectively. The measured $\Delta\omega$ was about 1–6 cm^{-1}. The lattice dynamically predicted relationship, $A \propto \omega_{TO}\Delta\omega$ (A = infrared absorbance), has been confirmed experimentally. The band assignments for PVDF form I reported in the previous paper (Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158) have been revised on the basis of the polarization character of the infrared and Raman spectra and by carrying out the normal coordinate treatment.

Recently poly(vinylidene fluoride) (PVDF) crystal form I has been proved experimentally to be a ferroelectric material.[1,2] In such ferroelectric substances, in general, the long-range dipole–dipole interaction plays a very important role in their physical properties and ferroelectric phase transition behavior.[3] However, it may be difficult to es-

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