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Structural study of syndiotactic polypropylene gel by solid-state high resolution ^{13}C n.m.r.

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The molecular conformation and the phase structure of syndiotactic polypropylene gel were studied by infra-red and solid-state high resolution ^{13}C n.m.r. spectroscopies. It was found that the *trans–trans–gauche–gauche* molecular conformation, that is most energetically stable in the bulk crystalline state of this polymer, is also formed in the gel. However, the methylene resonance lines of the gel observed in solid-state ^{13}C n.m.r. spectrum are somewhat different from that of the bulk crystal. The origin of this difference is attributed to a difference in the intermolecular interaction. The investigation of the phase structure revealed that the gel generally comprises three phases; the crystalline phase, noncrystalline amorphous phase, and crystalline–amorphous interphase in a similar manner to the bulk crystals. About 64% of solvent molecules in the gel are incorporated in the crystalline–amorphous interphase as bound solvent and another 34% are in the amorphous phase as free solvent. Copyright © 1996 Elsevier Science Ltd.

(Keywords: syndiotactic polypropylene; solid-state n.m.r.; phase structure)

INTRODUCTION

Interest in the gel structure of synthetic polymers from the scientific point of view has been growing for the last decade. The network structure formed in gel closely relates to macroscopic physical properties. Therefore, elucidation of the molecular structure is fundamentally important in order to clarify the whole scope of gel.

De Gennes has treated gel as a material in which the crosslinking point is constructed either by chemical reaction or physical coagulation[1]. The former makes an irreversible gel due to covalent bonds. The latter is classified into three models; crystalline, multi-helical structure and nodule structure. It is generally considered that the crystalline polymers form microcrystallite as crosslinking points. Syndiotactic polypropylene (sPP) is one of the most typical crystalline polymers. By recent improvement of polymerization catalysts, sPP with high stereoregularity has become available. As sPP forms a stable definable gel at room temperature, sample suitable for this work can be obtained[2]. The crystal structure and morphology of this polymer in the bulk state have been widely examined by X-ray and electron diffraction experiments[3–13], solid-state high resolution ^{13}C n.m.r. spectroscopy[14–17], and vibrational spectroscopy[18–20]. In relation to the molecular conformation, three types of helical structure are confirmed. The most stable form consists of a *trans*(*t*)–*trans*(*t*)–*gauche*(*g*)–*gauche*(*g*) molecular sequence (referred to as Form I or TTGG form), but a metastable form–all *trans* conformation (Form II or TT form)–is also formed by cold drawing. In addition, the formation of the *ttggtttttgg* sequence (Form III) is recently reported when the cold drawn film is exposed to a solvent vapour such as toluene[14]. To elucidate these molecular conformations of the bulk-crystalline sPP, solid-state high resolution ^{13}C n.m.r. spectroscopy has been found very effective, since the spectrum reflects sensitively the molecular conformation and coagulation. It is particularly stressed that the resonance of the methylene carbon exhibits strong dependence of the conformation. Characteristic chemical shift and splitting are observed for the sPP crystals. These are explained on the basis of the three bond interaction or the so-called γ-*gauche* effect[15,16]. That is, the splitting is attributed to a strong shielding by carbon atoms that are separated by three bonds and located at *gauche* position. For Forms I and III having the γ-*gauche* effect, the methylene carbon shows two or three split resonance lines, whereas Form II without the γ-*gauche* effect shows a single peak at the most downfield. Moreover, the methylene carbon resonance of isotactic polypropylene (iPP) in α-form crystal (monoclinic crystal) is observed as a doublet. This is because each methylene carbon may occupy one of two sites that differ in the magnetic environment[21–23]. Thus, the different crystal morphologies give rise to recognizably different spectra, enabling the n.m.r. technique to explore both intra- and intermolecular interactions.

In addition to the molecular conformation and packing, important information on the molecular mobility can be obtained by examining the magnetic relaxation phenomena of the resonance lines. The

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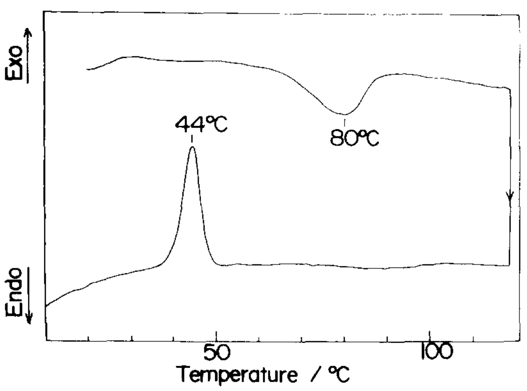

Figure 1 D.s.c. thermogram of sPP/*o*-dichlorobenzene gel (13.6 wt%). Heating and cooling rate was 5°C min^{-1}

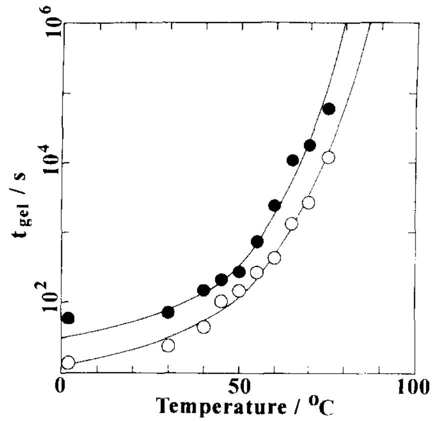

Figure 2 Gelation time at different temperatures measured by the tilting method for sPP/*o*-dichlorobenzene system: ○, 5 wt%; ●, 10 wt%

examination of longitudinal and transverse relaxations provides detailed information about the phase structure of crystalline polymers[23-25]. It is confirmed by Saito *et al.* that iPP crystal in α-form comprises three phases that differ in molecular conformation and mobility; the crystalline phase, noncrystalline amorphous phase and crystalline–amorphous interphase[23]. This paper deals with the molecular conformation and phase structure of the sPP gel. The experimental results of this gel are discussed, referring to the results mentioned above in relation to the sPP and iPP crystals.

EXPERIMENTAL

Samples

The sPP sample was supplied by Sumitomo Chemical Co. Ltd. The molecular weight was 8.2×10^6 g Z·mol^{-1} and the *racemic* triad was estimated to be 95%. The sample was dissolved completely in *o*-dichlorobenzene at 150°C and the gel samples were prepared by quenching in iced water. The concentration of the solution was 13.6 wt%. The gelation time was determined by tilting method. A solution sealed in a glass test tube was first heated to a temperature high enough to be free from gelation, and transferred in a thermostat kept at a given temperature, and the change in the fluidity of the solution was checked by tilting it until the solution no longer flowed. The gel was transparent when it was made and became somewhat translucent with time but further aspect change was not recognized. The TTGG crystal used as a reference was obtained from the melt-quenched film by annealing at 150°C for 2 h.

^{13}C n.m.r.

The ^{1}H dipolar decoupling/magic angle spinning (DD/MAS) ^{13}C n.m.r. measurements were carried out at a field strength of 4.7 tesla with the Bruker MSL 200 spectrometer at room temperature. The ^{13}C resonance frequency was 50.3 MHz, and the B_1 strength used was 65 kHz for both ^{13}C and ^{1}H. The MAS of 4 kHz was achieved by the double bearing system. Even for the gel sample, this MAS could be achieved without trouble. The thermal equilibrium spectrum as well as the longitudinal and transversed relaxation were studied according to the method used previously[24].

Infra-red spectroscopy

The infra-red spectra were taken using a JASCO *FT*i.r. 8300 spectrometer with 1 cm^{-1} resolution equipped with a DTGS detector.

RESULTS AND DISCUSSION

Sol–gel transition

A stable and homogeneous gel was formed in sPP/*o*-dichlorobenzene system at room temperature. A typical differential scanning calorimetry (d.s.c.) thermogram for a sPP/*o*-dichlorobenzene gel quenched at 0°C is shown in *Figure 1*. An endothermic peak at 80°C on heating and an exothermic peak at 44°C on cooling were recognized, corresponding to melting of the gel and re-gelation, respectively. The distribution of crystal size broadens the gel melting temperature. A simple one-step sol–gel transition suggests that the gel forms a homogeneous system. Inherently, the gelation process is similar to the crystallization from dilute solution except for the formation of a three dimensional network. The gelation strongly depends on concentration and temperature. In *Figure 2* the gel-forming time in logarithm is plotted against temperature. These data were obtained by the tilting method. The gelation time increases monotonically with temperature. In the vicinity of 80–90°C, depending on concentration, the gelation does not occur, even after long time periods. This temperature corresponds to the critical temperature for gelation. It is almost identical to the melting temperature observed by d.s.c. In the case of a syndiotactic polystyrene (sPS)/decalin system, two critical temperatures are observed[26,27], while in the present case, the sol–gel transition is not so complicated. In order to investigate the molecular structure under the same gelation condition, we used the gel sample quenched at 0°C in the following experiments.

Molecular structure formed in gel

Figure 3 shows the DD/MAS ^{13}C n.m.r. spectrum for the sPP/*o*-dichlorobenzene gel at the thermal equilibrium state. In order to obtain this equilibrium spectrum, a single pulse sequence $(\pi/2 - \mathrm{FID})_n$ was used (FID = free induction decay). The waiting time between pulses was fixed as more than five times the longitudinal relaxation time, T_{1C}, to ensure the sufficient recovery to the equilibrium magnetization. In this case, the ^{1}H – ^{13}C cross-polarization (CP) was not used to avoid the

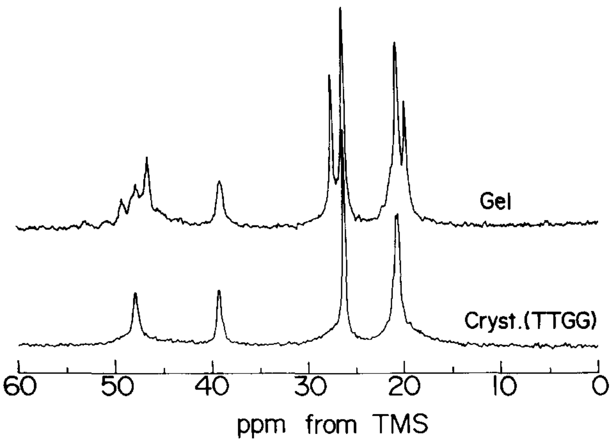

Figure 3 Equilibrium DD/MAS ^{13}C n.m.r. spectra of sPP/*o*-dichlorobenzene gel (13.6 wt%). The waiting time between the measurement pulses was fixed as 300 s, a long enough time to recover the equilibrium magnetization of all structural components. In the lower part the equilibrium spectrum of TTGG (Form I) crystal is shown as a reference

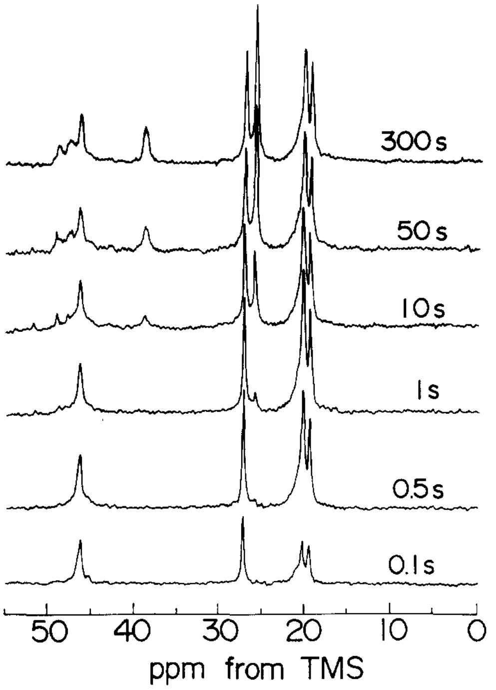

Figure 4 Actual spectra in the time progression of the saturation recovery (T_{1C} relaxation) of sPP/*o*-dichlorobenzene gel

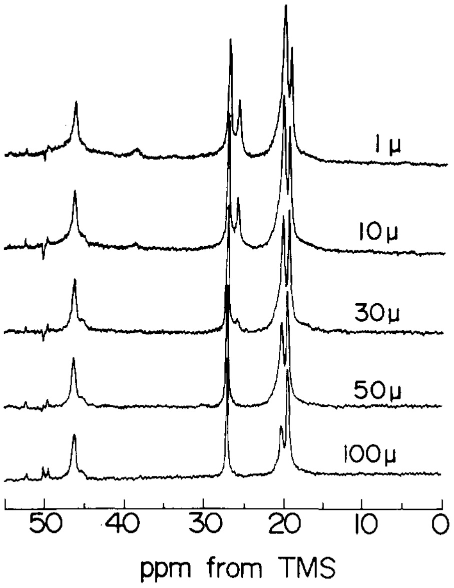

Figure 5 Actual spectra in the time progression of the transverse relaxation (T_{2C} relaxation) of sPP/*o*-dichlorobenzene gel, obtained by the pulse sequence used previously[24]

Table 1 Chemical shifts and T_{1C} values of sPP/*o*-dichlorobenzene gel (13.6 wt%) and TTGG crystal

	TTGG crystal			Gel		
	shift(ppm)	T_{1C} (s)	T_{2C} (ms)	shift (ppm)	T_{1C} (s)	T_{2C} (ms)
CH_3				19.9	0.3	14
	20.7[a]	0.2	0.077	20.6	0.3	0.052
	20.9[a]	0.2	0.077			
CH	26.2	30	0.022	26.2	23	0.010
				27.4	0.2	11
CH_2	39.1	63	0.014	39.0	58	0.012
				46.4	0.2	13
	47.7	63	0.014	47.7	53	0.015
				49.0	53	0.016

[a] The splitting of the methyl resonance was reported in detail in reference 16

complication that may arise from different CP efficiencies for different phases in the gel system. For comparison, the spectrum of the TTGG crystal (Form I) is also shown in the lower part of the figure. These equilibrium spectra are thought to reflect faithfully the contributions from all structural components in the samples. At first glance the spectrum for the gel is somewhat different from that of the TTGG crystal. Several additional resonance lines are recognized in the gel spectrum, that are not recognized in the TTGG crystal spectrum. These lines are to be assigned to polymer carbons, because the resonance lines from the solvent carbons, *o*-dichlorobenzene, are thought to appear in the range of ca. 130 ppm.

In order to examine the molecular conformation in the gel, we have to assign these resonance lines. First it can be plausibly assumed that the resonance lines at ca. 20 ppm are assigned to the methyl carbon, and those in the ranges of 25–30 ppm and 35–55 ppm to the methine and methylene carbons, respectively. To provide further detailed assignment of these lines we have examined the longitudinal and transverse relaxations. *Figure 4* shows a series of spectra obtained in the time progression of the saturation recovery pulse sequence. In this sequence the shorter T_{1C} contributions appear first and the longer T_{1C} contributions follow. *Figure 5* gives a series of spectra in the time progression of the transversed relaxation. The magnetization recovered in the direction of the static field by the saturation recovery pulse for 30 s was turned 90°, and after allowing the transverse relaxation for chosen times the FID was observed and the spectra were obtained by the Fourier transform. In this sequence the shorter T_{2C} contributions disappear first and the longer T_{2C} contributions remain longer. The T_{1C} and T_{2C} values were obtained by analysing these data. The values are summarized in *Table 1* together with those of the TTGG crystal. We can distinguish the resonance lines of the equilibrium spectra shown in *Figure 3*, referring to these time progression spectra and the T_{1C} and T_{2C} values.

First it is noted in *Figures 4* and *5* that the sharp resonance lines at 19.9, 27.4 and 46.4 ppm quickly appear on the saturation recovery and remain for a relatively long time on the transverse relaxation experiments. The T_{1C} and T_{2C} are 0.3 s and 14 ms for the 19.9 ppm line, 0.2 s and 11 ms for the 27.4 ppm line, and 0.2 s and 13 ms for the 46.4 ppm line, respectively, as seen in *Table 1*. These relaxation times are typical of the rubbery state of polymers or rubbery amorphous components in crystalline polymers. The chemical shifts, 19.9, 27.4 and 46.4 ppm, are almost identical to those of methyl, methine and methylene resonance lines in solutions of this polymer. Hence the resonance lines at 19.9, 27.4 and 46.4 ppm are assigned respectively to the methyl, methine and methylene carbons in the noncrystalline amorphous component of the gel. On the other hand, other lines are assignable to crystalline carbons, because these lines are generally associated with relatively long T_{1C} and very short T_{2C} that are identical to those of the TTGG crystal. Thus the lines at 26.2 ppm and at 39.0, 47.7 and 49.0 ppm are assignable respectively to the methine and methylene carbons in the crystalline component in the gel. The line at 20.6 ppm is also assigned to the methyl carbon in the crystalline component of the gel, because this is associated with a very short T_{2C} (0.052 ms) and the chemical shift of 20.6 ppm is very close to 20.7 ppm for the methyl carbon in the TTGG crystal. We note here that the T_{1C} values of the crystalline methyl carbon are as short as 0.2–0.3 s for both TTGG crystal and gel. Such a short T_{1C} value is also reported for the crystalline methyl carbon of iPP[23]. These short T_{1C} values could be a result of rapid molecular motion of the methyl carbon in the time scale of T_{1C} (in the order of the Larmor frequency of ^{13}C and ^{1}H, i.e. ca. 10^8 Hz) in the crystal lattice. The methyl group is thought to undergo a diffusional rotation such as 3-fold rotation even in the crystal lattice, holding the molecular conformation unchanged[28,29]. However, the T_{2C} is as short as 0.052 ms, because the molecular motion of the methyl carbon in the time scale of T_{2C} (ca. 10^6 Hz), relating to the molecular conformational change, is limited in the crystalline region.

As mentioned above, we could assign all lines appearing in the equilibrium spectrum for the gel. Now we consider the molecular conformation in the crystalline component of the gel. For the TTGG crystal two split lines are recognized for the methylene carbon at 39.0 and 47.7 ppm. This splitting can be the result of the γ-*gauche* effect as mentioned in the introductory section. It is semiempirically confirmed that the adjacent methine carbon separated by three bonds at the *gauche* position makes the methylene resonance shift by ca. 5 ppm upfield. The peak at 47.7 ppm is assigned to the methylene carbon of *tg–gt* sequence without such *gauche* methine carbons in the TTGG crystal, whereas the upfield 39.0 ppm line is assigned to the methylene carbon of the *gt–tg* sequence with two *gauche* methine carbons. On the other hand three distinguishable lines are recognized at 39.0, 47.7 and 49.0 ppm to the crystalline methylene carbon in the gel. The intensity ratio of the three lines is 1/2/3. The chemical shifts of the former two, 39.0 and 47.7 ppm lines, are the same as those of the TTGG crystal (Form I) and that of the last line at 49.0 ppm is identical to that of the TT crystal (Form II). The methylene chemical shift of Form III could split into three, corresponding to the methylene carbons in the *tt–tt*, *gt–tg* and *gt–tt* sequences. Nevertheless, the triple splitting of the methylene resonance of the gel cannot be attributed to the existence of a Form III crystal because of the lack of a 44 ppm line from the *gt–tt* sequence resonance with one γ-*gauche* effect. To confirm whether the gel structure consists of the mixture of TT and TTGG crystals or not, we have measured the infra-red (i.r.) spectra that are very sensitive to the molecular conformation. The number of normal vibrational modes drastically depends on the molecular conformation based on the selection rule of the symmetry species. Kobayashi *et al.* confirmed the vibrational modes assignable to the *ttgg* conformation in the i.r. spectrum for the gel from sPP/carbon disulfide system[2]. In this work, however, we have used *o*-dichlorobenzene as solvent. We have examined whether the gel structure depends on solvent. *Figure 6* shows the i.r. spectra of TT and TTGG crystals and the gel. Here the spectrum of gel was obtained by subtracting the contribution from *o*-dichlorobenzene by computer analysis. The differences in the number of detected i.r.-active bands between the TT and TTGG crystals reflect the number of monomeric units contained in the fibre period as well as the factor group symmetry. It is recognized that all vibrational modes of the gel are completely the same as TTGG crystal. This indicates that the conformation formed in the gel takes a *ttgg* sequence as reported for sPP/carbon disulfide gel. The absorption bands characteristic of TT crystal, such as those at 1234, 1131 and 830 cm^{-1}, cannot be recognized in the gel spectrum. This result is evidence that the two crystal forms, TTGG and TT, do not coexist in the gel.

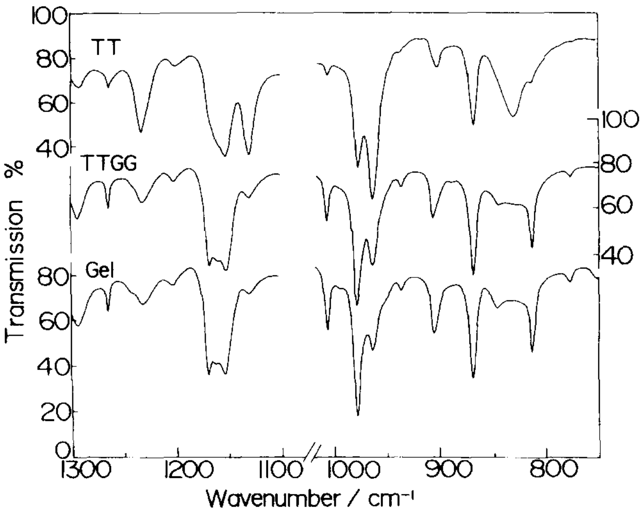

Figure 6 Infra-red spectra of TT crystal, TTGG crystal and sPP/*o*-dichlorobenzene gel (13.6 wt%). The spectrum of the gel shows only the contribution from the polymer, that was obtained by subtracting the contribution from the solvent component

A possible explanation for the results of ^{13}C n.m.r. and i.r. spectra observed in this work will be given by taking a molecular packing effect into account that can yield a triplet resonance to the methylene carbon in DD/MAS ^{13}C n.m.r. spectrum. Since the i.r. spectrum indicates the existence of only *ttgg* sequence, all split lines of the methylene carbon should be assigned to the *ttgg*

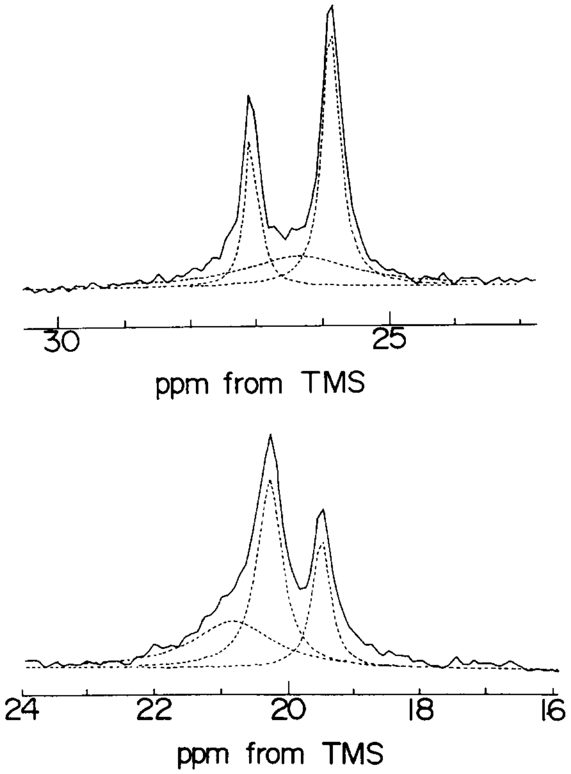

Figure 7 Component analysis of methine (upper) and methyl (bottom) resonances. The relatively narrow dotted Lorentzians centered at 26.2 and 20.6 ppm represent the contributions from the methine and methyl carbons in the crystalline phase, and those centered at 27.4 and 19.9 ppm represent the contribution from the respective carbons in the amorphous phases. The broad dotted Lorentzians centered at ca. 25.3 and 20.8 ppm represent the contributions from the respective carbons in the crystalline–amorphous interphase

sequence. It is assumed that the resonance due to the *tg–gt* sequence is further split into 47.7 and 49.0 ppm because of the molecular packing effect, and because the *gt–tg* sequence stays as a singlet at 39.0 ppm. Sozzani *et al.* observed the 49.0 ppm peak (50.2 ppm estimated by them) in an as-polymerized sample[15]. They did not regard it as the *tt–tt* conformation. Since the *tg–gt* methylene locates at the outer position of the helical structure of sPP, an enhanced interaction with neighbouring helical molecular chains is expected. Therefore there will be two distinct magnetic environments possible for the *tg–gt* methylene to yield the splitting. The splitting width of 1.3 ppm observed here for the gel is comparable to that in the case of α-crystal of iPP (1.0 ppm)[20,21]. This splitting is understood as being due to the existence of inequivalent sites for methylene carbons due to the molecular alignment in the crystal lattice. In the case of sPP gel, the same effect is predicted. Further structural investigation will be reported in the following paper.

Phase structures

It is confirmed by high resolution solid-state ^{13}C n.m.r. that iPP crystal consists of three phases; the crystalline, noncrystalline amorphous phase and crystalline–noncrystalline interphase[23]. We have analysed the ^{13}C n.m.r. spectrum to study the phase structure of sPP gel by a method similar to that used previously[23]. For this purpose the methine and methyl resonances are most pertinent because of the simplicity of the spectral shape.

Table 2 The phase fraction of sPP/*o*-dichlorobenzene gel (13.6 wt%)

	Crystalline	Noncrystalline	Interphase
CH	0.43	0.19	0.38
CH_3	0.44	0.22	0.34

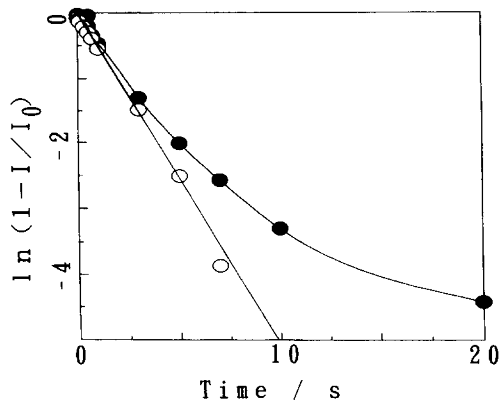

Figure 8 ^{13}C longitudinal relaxation of the 130 ppm resonance line of *o*-dichlorobenzene observed in saturation recovery pulse sequence. ●, Relaxation behaviour in gel; ○, relaxation behaviour in pure solvent

Figure 7 shows a line shape analysis of methine and methyl resonances of the DD/MAS ^{13}C n.m.r. spectrum, where a Lorentzian function is assumed for each component. The sharp Lorentzian components centred at 26.2 and 20.6 ppm, and 27.4 and 19.9 ppm are assignable to the methine and methyl carbons in the crystalline and amorphous phases, respectively, as discussed in the last section. In addition to these components, broad Lorentzian components are recognized centred at ca. 25.3 and 20.8 ppm for the methine and methyl carbons. It was confirmed by minutely examining their longitudinal and transverse relaxations shown in *Figures 4* and *5* that these components are associated with T_{1C} values as short as 0.2–0.3 s and very short T_{2C} values comparable to those of the crystalline phase. Hence these broad components are assigned to the methine and methyl carbons in the crystalline–amorphous interphase. We conclude that the sPP of the gel involves three phases, the crystalline, amorphous phases, and crystalline–amorphous interphase in a similar manner to the bulk crystal.

The mass fractions of these three phases are shown in *Table 2*. It is seen that the crystalline fraction is relatively small, at 0.43 or 0.44. This low level of crystallinity may arise from relatively strong molecular entanglement due to the network structure. This phase structure of the gel should be reflected on the mobility of the solvent that makes the gel. *Figure 8* shows the longitudinal relaxation for 130 ppm line of *o*-dichlorobenzene. The open circles indicate the data of the pure solvent and closed ones those of the gel. The relaxation of the pure solvent evolves exponentially with T_{1C} of 3.0 s, whereas that of the gel evolves nonexponentially. This indicates that there are some solvent molecules in the gel that differ in their mobility. The nonexponential decay including *i*th components follows the next equation

$$I = \sum_i I_{0i}[1 - \exp(-\tau/T_{1i})] \qquad (1)$$

Here τ is the variable delay time, I denotes the total intensity at τ and I_{0i} the intensities at $\tau = \infty$ for the *i*th

Table 3 The mass fractions of the bound and free solvent and those of the interphase and amorphous phase in the noncrystalline phases of the polymer

	Bound region (or interphase)	Free region (or amorphous phase)
Solvent[a]	0.70	0.30
Polymer[b]	0.64	0.36

[a] The mass fractions of bound and free solvents determined from equation (1)

[b] The mass fractions of polymer molecules in the two noncrystalline phases. The average of the values from CH and CH_3 data in *Table 2* is shown

component. T_{1i} is the T_{1C} for the *i*th component. $I_{0i}/\sum_i I_{0i}$ provides the mass fraction of the *i*th component. Using this relation the longitudinal relaxation in *Figure 8* could fit well with two relaxation terms. We have obtained two different T_{1C}s of 2.2 s and 9.2 s. In the gel, the existence of two kinds of solvent molecule referred to 'free solvent' and 'bound solvent' is well-known[30-32]. The two T_{1C}s obtained here are thought to correspond to those for these free and bound solvents. The shorter T_{1C} of 2.2 s is almost equal to that of the pure solvent. Hence this fraction corresponds to the solvent under free state. The other component with T_{1C} of 9.2 s can be assigned to 'bound solvent'. The mass fractions of these two components obtained by evaluating $I_{0i}/\sum_i I_{0i}$ are shown in *Table 3*. About 70% of the solvent molecules are in a bound state. The solvent molecules exist in the noncrystalline amorphous phase or the crystalline–amorphous interphase of sPP, because they cannot enter in the crystal lattice of the polymer. In the gel, around 60–70% of the noncrystalline polymer molecules consists of the crystalline–amorphous interphase as estimated from the data in *Table 2*. This mass ratio of polymer molecules between the noncrystalline amorphous phase and the crystalline–amorphous interphase roughly corresponds to the mass ratio between the free and bound solvent, as can be seen in *Table 3*. Therefore it can be concluded that the bound solvent is trapped in the interphase between crystalline and noncrystalline. Since the solvent molecules are strongly bound among polymer chains, the fluidity as a liquid should be restricted. In other words, the chain entanglement in the interphase plays an important role for the solvent molecules not to flow out from the network structure. The high percentage of interphase region is essential to hold the solvent in the network. However, the free solvent, which has no interaction from the surroundings, will be segregated from the gel (known as the syneresis phenomenon). If the polymer chain does not form a significant amount of interphase region, gelation will not occur since most of the solvent molecules are in a free state. Alternatively the aggregation of polymer chains will lead to a precipitation such as the crystal grown from dilute solution.

CONCLUSIONS

Syndiotactic polypropylene makes a thermoreversible physical gel consisting of crystal as a crosslinking point. It is found by solid-state high resolution ^{13}C n.m.r. that the molecular structure is different from the three crystal modifications known for the bulk crystal of this polymer. As for the regular chain sequence, it takes the same conformation as the TTGG crystal, which is the most stable in bulk crystal. The solid-state high resolution ^{13}C n.m.r. method is powerful for analysing the phase structure as well as the crystal structure. The existence of the intermediate phase between crystalline and non-crystalline amorphous phases is confirmed in the gel. The solvent molecules are classified into two states with different mobilities, free and bound. It is suggested that there is a close relationship between the interphase and the bound solvent.

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