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Investigation of the crystallization process of syndiotactic polypropylene quenched at 0°C from the melt or concentrated solutions by solid-state ^{13}C NMR spectroscopy

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Abstract

The crystallization process of syndiotactic polypropylene (sPP) quenched from the melt or concentrated solutions has been investigated by high-resolution solid-state ^{13}C NMR spectroscopy in order to make clear the formation of the planar zigzag form at 0°C. The sPP film just after quenching at 0°C from the melt is in the noncrystalline state, but when the film is left at room temperature, crystals with sPP in the t_2g_2 conformation are quickly produced. The ^{13}C NMR spectral shape of the CH_2 resonance line is similar to that of the sPP gels previously obtained. For the gels quenched at 0°C from concentrated solutions, T_{1C} and T_{2C} measurements reveal that segmental mobility remarkably decreases with increasing polymer concentration in the noncrystalline phase, whereas it stays unchanged in the crystalline phase as a result of lack of penetration of solvent molecules. Increase of viscosity in the noncrystalline phase results in the decrease of molecular mobility. In particular, molecular mobility is extremely restricted in the noncrystalline phase for the solvent-free sample, compared with the case of the gels. A line shape analysis of the CH_3 resonance line indicates that the trans fraction of the noncrystalline component is significantly increased above about 70 wt% concentration. These results lead to the conclusion that the molecular mobility in solutions below about 70 wt% is fast enough to take the almost random chain conformation as expected, but the sPP chains in solutions above about 70 wt% including in the bulk state tend to take trans-rich conformations, probably due to some kind of intermolecular interaction. As a result, crystallization from solutions with appropriate concentrations produces crystals with the most stable t_2g_2 sequences, whereas form III with the planar zigzag conformation is induced around 0°C in the solvent-free bulk state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polypropylene; Solid-state ^{13}C NMR; Crystallization

1. Introduction

It has been established that syndiotactic polypropylene (sPP) exhibits polymorphic structures. The most stable conformation is known to be the t_2g_2 sequence, and the crystal forms are proposed to be forms I and II that are, respectively, composed of antichiral and isochiral helices with the t_2g_2 conformation [1–12]. Another stable conformation is the planar zigzag (t_2) sequence. The crystal form with the t_2 sequence (form III) can be obtained under a special condition, that is cold-drawing of the quenched sample [13–16] or by spontaneous crystallization around 0°C [17–21]. The former method was first reported by Natta et al. [13] and the latter was recently found by our group [17–19]. Our finding is that form III is spontaneously crystallized around 0°C from highly trans-rich sPP chains after quenching from the melt. However, the crystal forms produced around 0°C strongly depend on the crystallization temperature: Infrared spectra revealed that form I is also crystallized above 5°C from the highly trans-rich chains. Moreover, the degree of crystallinity of form I is increased with increasing temperature, while the maximum degree of crystallinity is obtained at 0°C for form III [19]. Such a difference in crystallization process at different temperatures may be explained by the difference in transition rate between the trans and gauche conformations [21]. As the transition rate is of the order of 100 Hz around 10°C, conformational changes more rapid than this rate in the trans-rich noncrystalline chains seem to be preferable for the crystallization of form I with the t_2g_2 sequence.

Crystallization from a solution is another important process for the formation of the regular structure from the noncrystalline state. In most cases, crystallization from a dilute solution provides single crystals, when the radius of gyration of a polymer molecule is sufficiently smaller than

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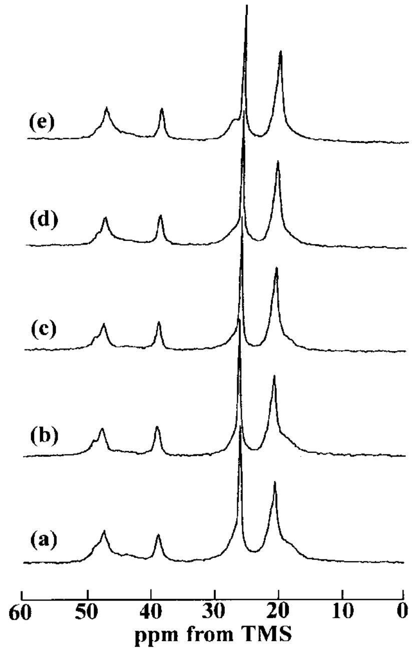

Fig. 1. CP/MAS ^{13}C NMR spectra of MQ5 at different temperatures: (a) 23°C; (b) 40°C; (c) 60°C; (d) 70°C; and (e) 80°C.

the average distance between two neighboring molecules. For concentrated solutions, the system is solidified by the formation of gels with a three-dimensional network structure. Since sPP is a typical crystalline polymer, the cross-linking points should be constructed from crystallites. Therefore, such gelation is regarded as a kind of crystallization process and the difference between gelation and crystallization will appear as some difference in crystal form or in morphology. The high-resolution solid-state ^{13}C NMR spectrum of sPP gels is characterized by the split profile of the methylene carbon [22]. We pointed out that the t_2g_2 conformation is formed in the gels but the crystal structure cannot be interpreted in terms of either of the crystal forms previously reported.

In this paper, the crystallization of sPP quenched at 0°C from concentrated solutions or from the melt is investigated by high-resolution solid-state ^{13}C NMR spectroscopy. The purpose of this investigation is to make clear the crystallization process for form III with the planar zigzag conformation.

2. Experimental section

2.1. Samples

The sPP sample was supplied by Sumitomo Chemical Co. Ltd. The molecular weight and the racemic triad (rr) content are 8.2×10^6 and 95%, respectively. sPP gels were prepared by quenching each sPP solution in a test-tube into ice-water after completely dissolved in *o*-dichlorobenzene at 150°C. Melt-quenched films were also prepared by quenching sPP films with a thickness of about 100 μm into ice-water from the melt at 150°C and then leaving them at room temperature after being kept in ice-water for 5 min. This sample is referred to as MQ5.

2.2. Solid-state ^{13}C NMR measurements

Solid-state ^{13}C NMR measurements were carried out on a Bruker MSL 200 spectrometer at a static magnetic field of 4.7 T. Magic angle spinning (MAS) of 3 kHz was achieved by the double air bearing system. The ^{1}H and ^{13}C radio-frequency field strengths $\gamma B_1/2\pi$ were 62.5 kHz. CP/MAS ^{13}C NMR spectra were collected with a contact time of 1 ms and a recycle time of 4 s. Fully relaxed dipolar decoupling (DD)/MAS ^{13}C NMR spectra were also obtained by the $\pi/2$ single pulse sequence, in which the recycle time was set to 300 s. The ^{13}C chemical shifts relative to tetramethyl silane (Me_4Si) were determined by using the peak at 176.03 ppm for the carbonyl carbon of glycine crystals as an external reference. The sample temperature was calibrated by the chemical shifts of the CH_2 and OH protons for ethylene glycol [23–25]. No window function was employed to enhance the signal/noise ratio.

3. Results and discussion

3.1. Spectral features of melt-quenched films

The sample held in ice-water for a few hours after quenching from the melt produces form III with the t_2 conformation [17–21]. When the period of soaking in ice-water is as short as 5 min, the polymer chains are in the noncrystalline state at 0°C. However, the sample taken out of the ice-water and left at room temperature was found to produce form I crystals composed of antichiral helices with the t_2g_2 conformation by wide-angle X-ray diffractometry [17,18]. Fig. 1 shows CP/MAS ^{13}C NMR spectra measured at different temperatures for the sPP sample (MQ5) obtained by the same procedure. This process corresponds to the result reported by Sozzani et al. [7] As is clearly seen, the methylene resonance line does not show the typical doublet for form I [26] crystallized at higher temperatures from the melt, but it additionally contains a broad downfield shoulder at about 49 ppm at each temperature. This chemical shift corresponds to that of the planar zigzag form, which is reported to be unstable over 50°C. However, this component can be seen even at 80°C as shown in Fig. 1, indicating it is not due to the planar zigzag form. Such an additional peak was also observed for sPP gels quenched into ice-water from the *o*-dichlorobenzene solution at 150°C [22].

Fig. 2 shows the curve fitting analysis of the CH_2 resonance line observed for MQ5 at room temperature by DD/MAS ^{13}C NMR spectroscopy. Here, the equilibrium magnetization of the CH_2 carbons was used for the quantitative analysis. The peak at 47.0 ppm is due to noncrystallinity.

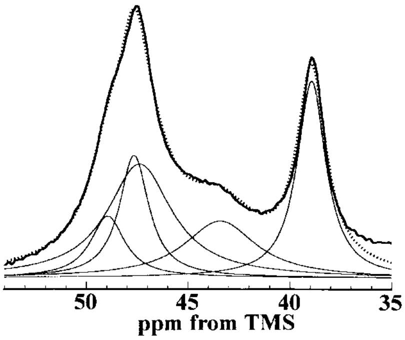

Fig. 2. Curve fitting analysis of the CH_2 resonance line for MQ5. The spectrum was obtained at room temperature by CP/MAS ^{13}C NMR spectroscopy.

This spectral shape is characterized by three components at 49.0, 47.7 and 39.0 ppm. The same crystalline contributions were also found for sPP gels prepared by quenching the moderately concentrated solutions from 150°C into ice-water [22]. The split into three lines was explained by intra- and intermolecular interactions as follows: the peaks at 39.0 and 47.7 ppm are, respectively, assigned to the CH_2 carbons with and without the γ-gauche effect, in good accordance with the previous assignment [26] for the doublet observed for the sPP samples crystallized at higher temperatures from the melt. However, the peak at 49.0 ppm, which may be due to packing effects, is assumed to be without a γ-gauche effect. The broad peak at 44.0 ppm corresponds to the chemical shift with one γ-gauche effect. This component might be assumed to be due to an intermediate phase between crystalline and noncrystalline. At this point the crystal form is unclear, but the crystallization mechanism is worth discussing for both the melt-quenched film and the gels prepared from the solution. In order to elucidate the crystallization mechanism for form III, the molecular mobility of the gels with various concentrations has been investigated.

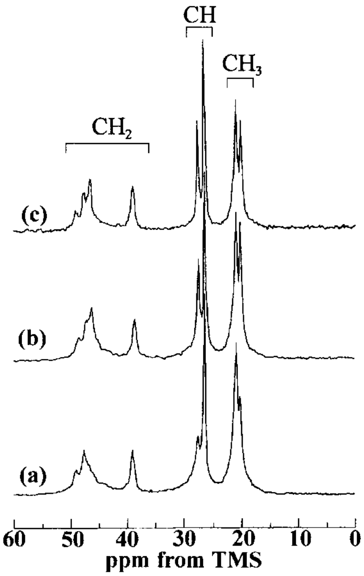

Fig. 3. Fully relaxed DD/MAS ^{13}C NMR spectra of sPP gels prepared from solutions with different polymer concentrations: (a) 20 wt%; (b) 49 wt%; and (c) 70 wt%.

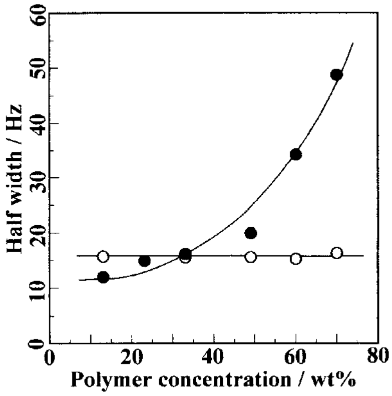

Fig. 4. Half-width of the CH resonance line as a function of the polymer concentration of the solution that was used for the sPP gel preparation. ((○) crystalline; ((●) noncrystalline.

3.2. Molecular mobility of the sPP gels depending on the polymer concentration

Fig. 3 shows fully relaxed DD/MAS ^{13}C NMR spectra measured at room temperature for sPP gels prepared from *o*-dichlorobenzene solutions with different concentrations. The spectral shape shows almost no dependence on soaking time in ice-water unlike the case of melt-quenched films where form III is spontaneously crystallized with increasing soak time. Even after annealing at room temperature, no change in spectral shape is observed in each gel sample. The resonance lines at 46.4, 27.4 and 19.9 ppm, whose intensities evidently decrease with increasing concentration, are assigned to the noncrystalline component of the CH_2, CH, and CH_3 carbons, respectively. The crystalline component for the CH_2 resonance line is characterized by three peaks appearing at 49.0, 47.7 and 39.0 ppm. The chemical shifts of these lines are in good agreement with those observed for MQ5.

In Fig. 4, the half-widths of the crystalline and noncrystalline components for the CH resonance lines shown in Fig. 3 are plotted against the polymer concentration. Here, the separation of the CH lines into these two components was readily conducted by the line shape analysis assuming Lorentzian curves for the respective contributions. Remarkable line broadening can be seen for the noncrystalline component with increasing concentration, whereas the line width for the crystalline component remains essentially constant. The latter fact indicates that the local orientation of sPP chains undergoes no change in the crystalline region with changing polymer concentrations for the gel preparation. In general, line widths of DD/MAS ^{13}C spectra reflect the statistical distribution of the local structure or its average by molecular motion. Although the noncrystalline

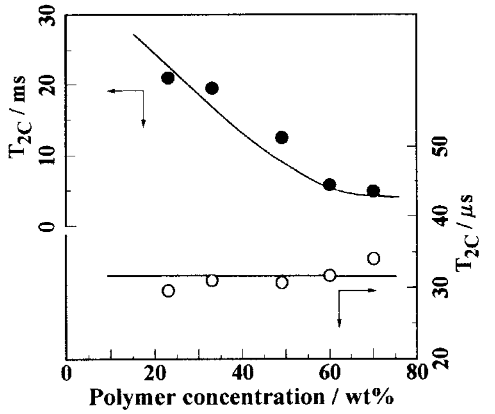

Fig. 5. T_{2C} value of the CH resonance line as a function of the polymer concentration of the solution that was used for the sPP gel preparation. ((○) crystalline; ((●) noncrystalline.

component consists of different conformational isomers, the resonance lines ascribed to these contributions may be averaged in the gel state swollen with a solvent by the fast exchange motion among them. Therefore, in order to examine the origin of line broadening for the noncrystalline component, ^{13}C spin–spin relaxation times (T_{2C}) have been measured under a condition of no ^{1}H dipolar decoupling during the T_{2C} relaxation period by the spin echo method modified for solid-state measurements.

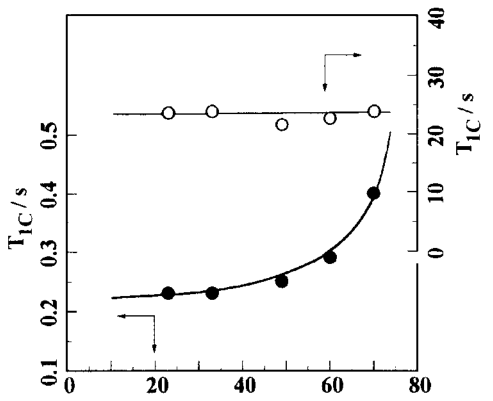

Fig. 6. T_{1C} value of the CH resonance line as a function of the polymer concentration of the solution that was used for the sPP gel preparation. ((○) crystalline; ((●) noncrystalline.

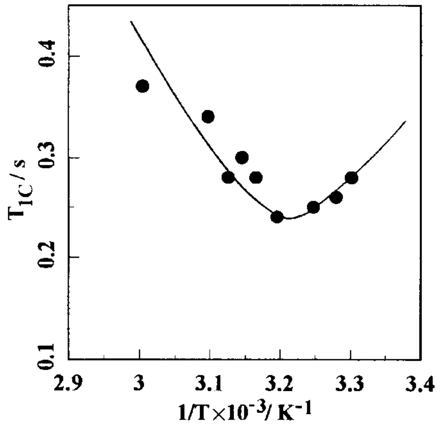

Fig. 7. Temperature dependence of the T_{1C} value for the noncrystalline component of the CH resonance line.

Fig. 5 shows the plot of T_{2C} as a function of polymer concentration for the gel preparation. According to the single-correlation-time theory (for example Ref. [27]), a longer T_{2C} value corresponds to less molecular mobility. Therefore, the noncrystalline component is found to decrease markedly in molecular mobility with increasing concentration as shown in Fig. 5. Spin-lattice relaxation measurement is another powerful technique to obtain information about molecular mobility associated with a rate around about 10^8 Hz. The dependencies of spin-lattice relaxation times (T_{1C}) on the polymer concentration are shown for the crystalline and noncrystalline components of the CH carbons in Fig. 6. Here, these T_{1C} values were measured by the saturation recovery pulse sequence. The T_{1C} for the noncrystalline component is found to increase with increasing polymer concentration, whereas T_{1C} stays almost constant for the crystalline component. According to the Bloembergen–Purcell–Pound (BPP) theory (for example Ref. [27]), T_{1C} has a minimum value at a correlation time corresponding to the inverse resonance frequency. It is therefore important to clarify on which side against the T_{1C} minimum is located the state defined under the present experimental condition. The temperature dependence of T_{1C} is shown for the noncrystalline component of the CH resonance line in Fig. 7. As is theoretically expected, a T_{1C} minimum can be observed at about 40°C. This result indicates that the state at room temperature corresponds to the lower temperature side against the T_{1C} minimum shown in Fig. 7. Therefore, the increase in T_{1C} with increasing polymer concentration can be interpreted as a decrease in molecular mobility.

As revealed in the previous paper [22], the solvent molecules are unable to enter into the crystalline region. This fact leads to a constant T_{1C} for the crystalline component irrespective of the polymer concentration for the gel preparation as shown in Fig. 6. All solvent molecules are distributed in the noncrystalline phase. The mobility of solvent molecules in the noncrystalline phase depends on the crystallinity, because the conformational restriction of the noncrystalline segments may be affected by the coexisting crystallites.

DD/MAS ^{13}C NMR spectra are very convenient to determine the degrees of crystallinity for various polymers (for example Refs. [20,28,29]). Line shape analysis has been applied to the CH resonance line for each gel sample shown in Fig. 3 as described above. Fig. 8 shows the degrees of crystallinity obtained as integrated fractions for the crystalline component by this analysis. It is found that the degree of crystallinity stays almost constant independent of the polymer concentration at which the gels were crystallized.

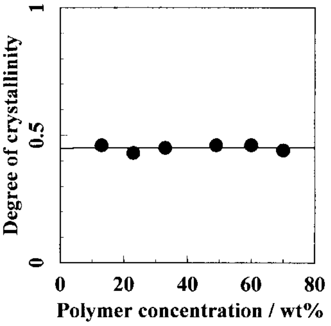

Fig. 8. Degrees of crystallinity estimated by curve fitting analysis of the CH resonance line for sPP gels prepared from solutions with different polymer concentrations.

Since the T_{1C} value also shows no dependence on the concentration as shown in Fig. 6, the number and the size of crystallites produced will be almost the same for sPP gels prepared in this range of concentration. This fact indicates that the actual concentration in the noncrystalline phase in the gels is closely related to the initial concentration of the solution before gelation. For the gels prepared from a solution with a higher concentration, the concentration of segments becomes higher in the noncrystalline phase. This is the reason why the molecular mobility as characterized through T_{2C} and T_{1C} measurements is lower for the gels prepared from the solutions with higher concentrations.

For the noncrystalline CH carbon for MQ5, the T_{1C} value was estimated to be 3.4 s, which is much longer than the T_{1C} values for different gels shown in Fig. 6. Therefore, the molecular mobility is much more restricted compared with the gels because of the absence of solvent molecules. This result is very important to elucidate the formation of form III with the t_2 conformation at 0°C as described later.

3.3. Molecular conformation in the noncrystalline phase

The CH_3 resonance line of sPP is known to reflect the conformation of the main chain through the γ-gauche effect. In the case of the CH_3 line, the γ-gauche effect seems to appear differently compared to the case of the main chain CH_2 line. When the main-chain CH_2–$CH(CH_3)$ bond adopts the trans conformation, the CH_3 and γ-CH carbons adopt the gauche position. Therefore, the CH_3 carbon receives the γ-gauche effect and its resonance line shifts downfield compared to the case of the gauche conformation for the CH_2–$CH(CH_3)$ bond. Fig. 9 shows the DD/MAS ^{13}C NMR spectra of the CH_3 carbons measured at room temperature for MQ5 and the sPP gels prepared from the 50 and 90 wt% solutions. The CH_3 resonance line is resolved into three Lorentzian curves in each sample as shown in this figure. A somewhat sharp constituent line at 21.5 ppm, which is referred to as line II according to the previous assignment [20], should be assigned to the CH_3 carbon with the tg or gt conformation for the CH_2–$CH(CH_3)$– CH_2 bond. Since form I crystals with the t_2g_2 conformation were confirmed to be produced in the gels [22], this line can be ascribed to the contribution from form I crystals. In contrast, the assignment of the broader constituent line (line III) at 21.6 ppm is not straightforward at present. No such contribution was found to exist for the form III samples crystallized at 0°C or the form I samples crystallized from the melt [20,21]. Here, this component is simply called the medium component because this component may have medium properties between the crystalline and noncrystalline components. The average conformation is almost the same as that for the form I crystals but there may be some distortion of the conformation and/or irregularity in chain packing compared to the case of the crystalline component. Such differences may be due to the penetration of the solvent molecules in this component, while all solvents are excluded out from the crystalline region. It should also be noted that the chemical shifts of these two lines around 21.5 ppm stay almost constant for these different samples.

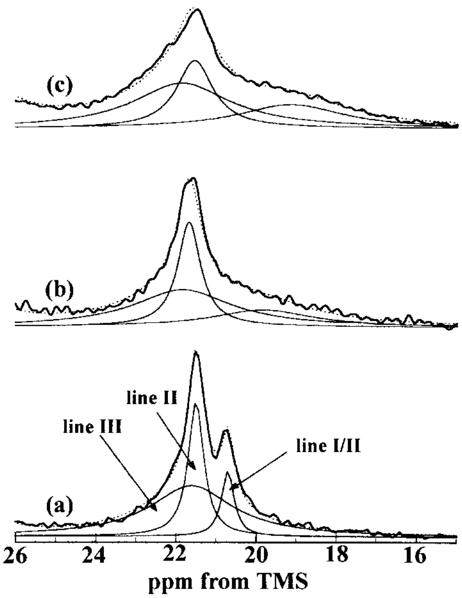

Fig. 9. Curve fitting analysis of the CH_3 resonance line for the sPP gels prepared from the solutions with different concentrations and melt-quenched films: (a) 50 wt%; (b) 90 wt%; and (c) MQ5. These spectra are fully relaxed DD/MAS ^{13}C NMR spectra.

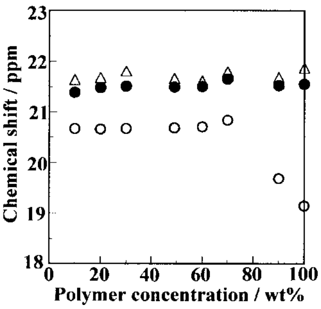

Fig. 10. Concentration dependencies of the chemical shifts for the different components appearing in the CH_3 resonance lines shown in Fig. 8. (○) line I/II; (●) line II; (△) line III.

In contrast, the most upfield constituent line, which is referred to as line I/II because of the reason described later, greatly shifts upfield with increasing polymer concentration, as is seen in Fig. 9. In Fig. 10, the chemical shift of line I/II thus obtained is plotted against the polymer concentration together with the results for lines II and III. The marked upfield shift of line I/II is found to be induced above 70–80 wt%, whereas the chemical shift values stay almost constant for lines II and III. According to the results of the similar line shape analysis for the form III samples crystallized at 0°C [18,20,21], line I/II should be assigned to the noncrystalline CH_3 carbons that undergo the rapid tt–tg or tt–gt exchange motion for the CH_2–$CH(CH_3)$– CH_2 bond. Here, line I is assigned to the CH_3 carbons associated with the tt conformation. Moreover, the upfield shift of line I/II indicates the increase in trans fraction for the noncrystalline segments. In fact, the trans fraction is found to increase from 0.57 to 0.73 in the noncrystalline phase with increasing polymer concentration by the estimation using the two-site exchange model.

Such an extraordinarily high trans fraction was also observed for the noncrystalline sPP at 0°C just after quenching from the melt [18] and for the noncrystalline component included in the form I and form III samples below about 50°C [21]. Although the cause of the trans-rich conformation for sPP chains at lower temperatures is not yet clarified at present, a marked decrease in trans fraction to the normal value expected for the sPP melt was observed at 20–50°C [21]. Some intermolecular interactions producing the trans-rich conformation may be reduced probably due to the enhanced molecular motion, as is suggested by ^{13}C spin–spin relaxation measurements in this temperature region [21]. In the case of sPP gels shown in Figs. 9 and 10, solvent molecules will promote the segmental motion in the noncrystalline region even at room temperature and as a result the trans fraction will be reduced with decreasing polymer concentration as seen in Fig. 9. The solvent effect on the chain conformation in sPP gels seems to correspond to the temperature effect in bulk sPP samples.

These results can be applied to the interpretation of the crystallization mechanism for form III with the t_2 conformation. Just after quenching from the melt, the molecular mobility of chains with the trans-rich conformation is too slow to take the stable t_2g_2 conformation. The aggregation among neighboring trans-rich chains may induce the crystallization of form III with the t_2 conformation. If there exist some amount of solvent molecules, the transition between trans and gauche conformations will be enhanced with ease. As a result, form I crystals with the t_2g_2 conformation may be formed in the presence of appropriate amounts of solvent. We reported that the crystallization at 0°C from the melt produces form III crystals with the t_2 conformation, while form I with the t_2g_2 conformation is preferentially grown at room temperature [17–19]. When the noncrystalline sample composed of trans-rich chains is left at room temperature, the thermal enhancement of molecular mobility induces the crystallization of form I with the t_2g_2 sequence.

4. Conclusions

The crystallization of sPP quenched from the solvent-free system and concentrated solutions was investigated by high-resolution solid-state ^{13}C NMR spectroscopy. The film left at room temperature after quenching at 0°C from the melt shows the characteristic ^{13}C NMR spectral profile similar to the case of the gels prepared from solutions, indicating the production of the same crystal structure. The noncrystalline phase in the gels formed from solutions contains a significant amount of gauche sequence because the chain mobility is fast enough to form the almost random chain conformation. The sample without solvent molecules tends to take the trans-rich sequences in the noncrystalline phase around room temperature. This will lead to the crystallization of form III with the planar zigzag form at lower temperatures.

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