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Normal mode analysis of syndiotactic polypropylene ($T_2G_2T_6G_2$) form

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Abstract

Syndiotactic polypropylene of all-*trans* form is transformed to ($T_2G_2T_6G_2$) form (new form) on exposing to xylene vapor under tension. This new form was characterized by infrared spectra and normal mode analysis. By increasing the *gauche* component from the all-*trans* to the new form, the infrared intensities of some bands increase. The potential energy distributions (PED) and **L** vectors for six monomers, which compose the repeating unit, were investigated. As a result, the PED and **L** vectors of the conformation-sensitive bands were found to be localized at the *gauche* position. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polypropylene; Normal mode analysis; Infrared spectra

1. Introduction

Syndiotactic polypropylene has three crystalline forms, i.e. the helical form of $(T_2G_2)_2$ conformation in the orthorhombic cell of the space group $C222_1$ [1–3], the planar-zigzag form of all-*trans* in the orthorhombic cell of the space group $P2_1cn$ [4], and the new form of ($T_2G_2T_6G_2$) in the triclinic cell of the space group $P1$ [5]. These forms have the repeating unit of 7.5, 5.06, and 11.60 Å, respectively. In 1991, Chatani et al. found the third form. In order to characterize these crystalline forms, vibrational spectroscopic studies are preferable. The infrared study of the former two forms has been performed on the basis of normal mode analyses by Schactschneider and Snyder in 1965 [6]. In this study, we made a normal mode analysis on the third form (new form) and characterized its infrared spectrum.

2. Experimental

Syndiotactic polypropylene was supplied from Mitsui Chemicals, Inc. The M_n was 78,000 ($M_w/M_n = 1.92$) and the pentad fraction measured by ^{13}C NMR was 0.946. The sample of the new form was prepared as follows. A film specimen of the $(T_2G_2)_2$ form was cast from xylene solution. A uniaxially oriented film of planar-zigzag form was obtained by stretching the melt $(T_2G_2)_2$ film in ice water. This oriented film having the all-*trans* conformation was exposed to xylene vapor under tension at 40 °C for about two days. Appearance of the new form was confirmed by infrared spectra and X-ray diffraction. The infrared spectra were measured by a JASCO IR-810 or a JEOL JIR-100 FT-IR spectrophotometer at room temperature.

3. Results and discussion

Syndiotactic polypropylene has three molecular forms as shown in Fig. 1. The left is the $(T_2G_2)_2$ form which is the most stable at ambient condition. The middle is the all-*trans* form which is prepared from the $(T_2G_2)_2$ form by cold drawing. The right is the ($T_2G_2T_6G_2$) form found by Chatani et al. in 1991 [5]. We first investigate the process of the new form formation by infrared spectra.

Fig. 2 shows the time dependence of the infrared spectra in the 600–1600 cm^{-1} region on exposing to xylene vapor from 0 to 108 h. The top spectrum is ascribed to the all-*trans* form. By monitoring the X-ray patters, we confirm that the all-*trans* form gradually changes to the ($T_2G_2T_6G_2$) form after 48 h and finally arrives at the $(T_2G_2)_2$ form after 200 h. Prominent spectral changes depending on exposing time are found as follows. The bands at 1233 and 1130 cm^{-1} appear fairly strongly at 0 h, but their intensities gradually

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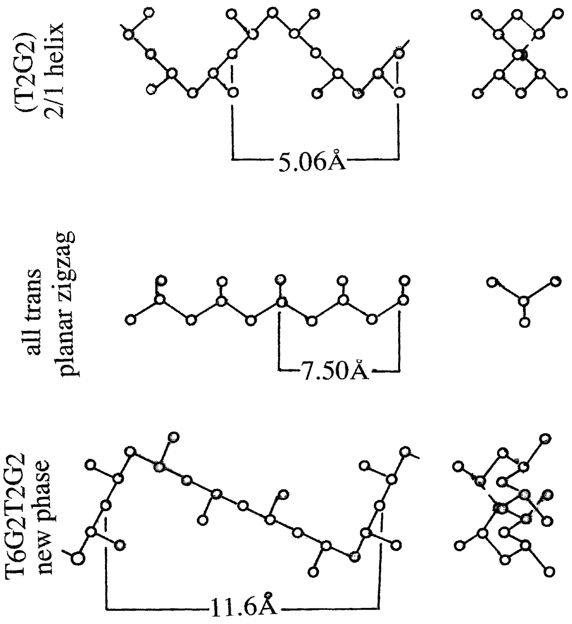

Fig. 1. Three molecular forms of syndiotactic polypropylene. Top: $(T_2G_2)_2$ form, middle: all-*trans*, and bottom: $(T_2G_2T_6G_2)$ form.

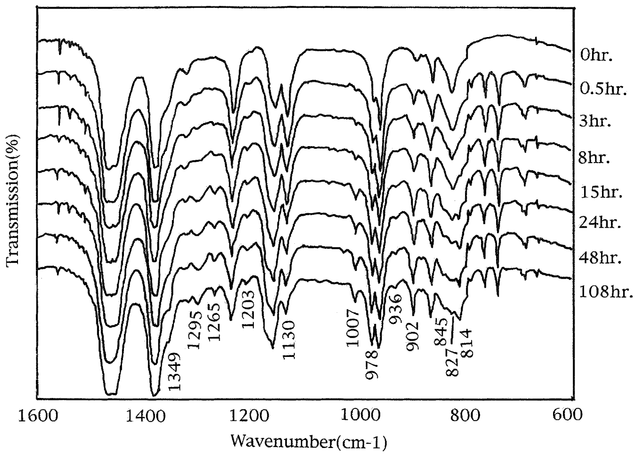

Fig. 2. Changes of infrared spectra of syndiotactic polypropylene from the all-*trans* to new phase on exposing to xylene vapor at 40 °C.

decrease with exposing time. The appearance of new peaks or intensity which increases with exposing time are observed at 1349, 1295, 1265, 1203, 1007, 978, 936, and 902 cm^{-1}. A single band at 829 cm^{-1} splits into four bands at 847, 827, 814 cm^{-1}, which finally converge to a band at 812 cm^{-1} (Fig. 3). The sharp bands observed below 800 cm^{-1} are ascribed to xylene molecules. After exposing the specimen at ambient condition in air, these xylene bands disappear, indicating that the compound is not an inclusion one. Xylene vapor just stabilizes the polymer chains to more stable conformation. The vacant space evaluated from unit cell volume (covalent volume of polymer molecules) are 269, 445, and 550 $Å^3$ for the all-*trans*, $(T_2G_2T_6G_2)$, and $(T_2G_2)_2$ forms, respectively. This may indicate that the xylene vapor is absorbed by the all-*trans* molecule first and forms inclusion compound at a moment. van der Waals interaction between the polymer molecule and xylene molecule repulsively affects them, and the interchain distances become larger, and results in the $(T_2G_2T_6G_2)$ conformation. The transition from $(T_2G_2T_6G_2)$ to $(T_2G_2)_2$ form may be explained by the same mechanism. Finally, xylene molecules are excluded from the crystalline region to the amorphous region and vapor. Fig. 3 shows the spectra ascribed to the all-*trans* (top), $(T_2G_2T_6G_2)$ (middle), and $(T_2G_2)_2$ (bottom) forms. The spectrum of the $(T_2G_2T_6G_2)$ form shows additional bands ascribed to the other two forms.

In order to characterize the infrared spectrum of the $(T_2G_2T_6G_2)$ form, we carried out a normal mode analysis by the Wilson GF matrix method using an IBM RS/6000-580 computer. The Cartesian coordinates are defined as follows. The CC bond length is 1.54 Å and CH is 1.093 Å, and all angles of the CCC, CCH, and HCH are assumed to be tetrahedral. The internal coordinates are defined as shown in Fig. 4. The matrix was not factored with the symmetry coordinates. Hence, the potential energy distribution and **L** vector components in the calculated results are based on the internal coordinates. All diagonal and off-diagonal valence force constants were transferred from those of Ref. [6]. The observed and calculated frequencies, and the potential energy distributions (PED) are listed in Table 1. The agreements between the observed and calculated frequencies are satisfactory.

In order to characterize the new bands which appeared for the $(T_2G_2T_6G_2)$ form, we evaluate the PED and the **L** vectors in the 800–1500 cm^{-1} region for each monomer unit. This region is sensitive to the conformational changes [7]. The PEDs are related to the force constants, and therefore to the frequencies. **L** vectors are related to the band intensities. The repeating unit of the new form consists of six monomer units. We number the units from one to six as shown in Fig. 5. Figs. 6–9 show the calculated results of PED and **L** vectors, respectively. The observed and calculated frequencies are listed at the left side. The α, δ, etc. shown at the top of the figures are the internal coordinates defined in the footnote of Table 1. Each square contains six vertical lines. These lines correspond to the monomer units from one (left side) to six (right side). Full scales are 50% and 1.5 for the PED and the **L** vectors, respectively. The monomers 1, 2, 5, and 6 contain the *gauche* conformation (TG). The monomers 3 and 4 are ascribed to the *trans* conformation (TT). Hence, if the PED and **L** vectors for the observed band, which is ascribed to the monomer 1, 2, 5, or 6 are large, this band is regarded as a *gauche* band, and if those ascribed to 3 and 4 are large, this band is assigned to *trans* band. For example, a band observed at 1455 cm^{-1} is associated with large PED at the

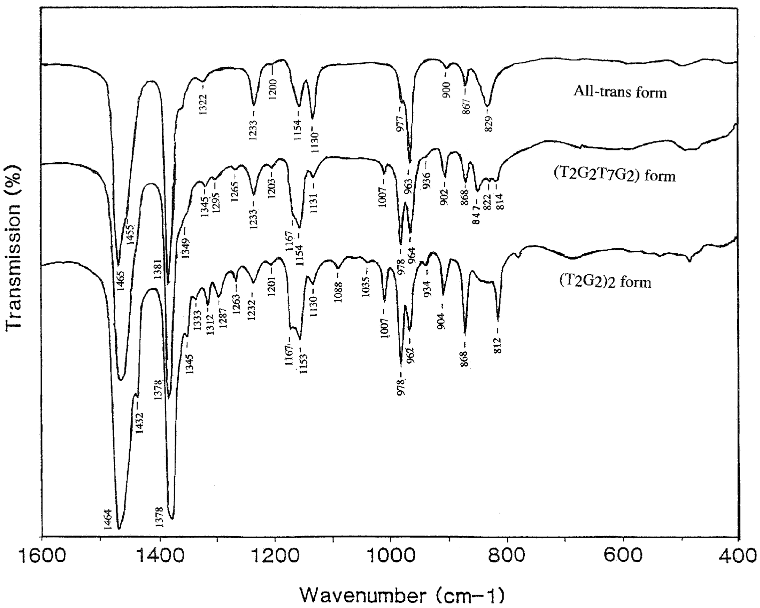

Fig. 3. Infrared spectra of three crystalline forms. Top: all-*trans*, middle: ($T_2G_2T_6G_2$) form, and bottom: (T_2G_2)$_2$ form.

monomers 2 and 6 and with large **L** vectors at the monomers 1, 2, 5, and 6 indicating that this band is a *gauche* band. The 1203 cm^{-1} band is associated with large PED at the monomers 3 and 4. This band is, therefore, regarded as a *trans* band. The summary of the characteristic bands is shown in Table 2, where *G* means *gauche* band, *T* means *trans* band, and – means that the band is not definitely characterized to a *gauche* band or a *trans* band. As described earlier, the intensities of the *gauche* bands increase as the structural changes occur from the all-*trans* to the ($T_2G_2T_6G_2$) form, and to the (T_2G_2)$_2$ form. However, the intensities of the *trans* bands decrease as the structural changes occur. In the assignment of Table 2, band intensities do not change remarkably. The most of the bands show consistent spectral behavior as described

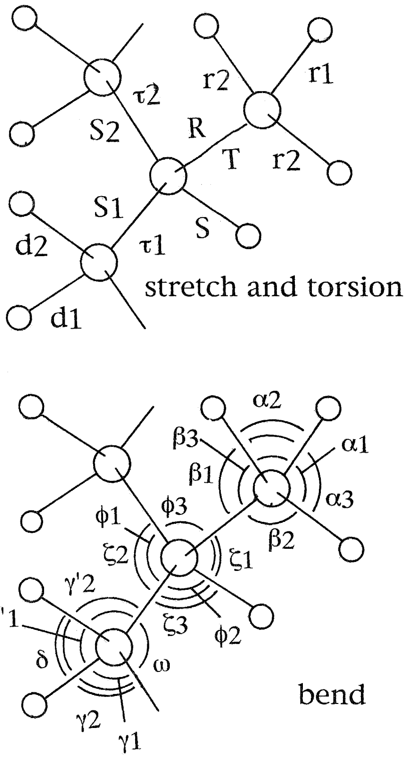

Fig. 4. Definition of internal coordinates. Top: stretch and torsion, and bottom: bend.

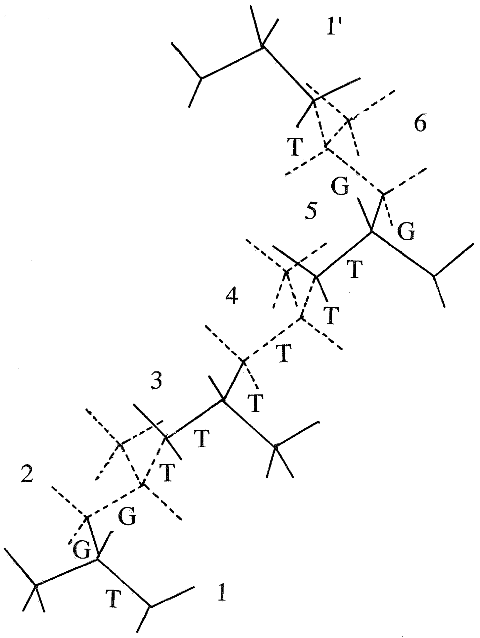

Fig. 5. Numbering of monomer units in one repeating unit of the ($T_2G_2T_6G_2$)$_2$ form.

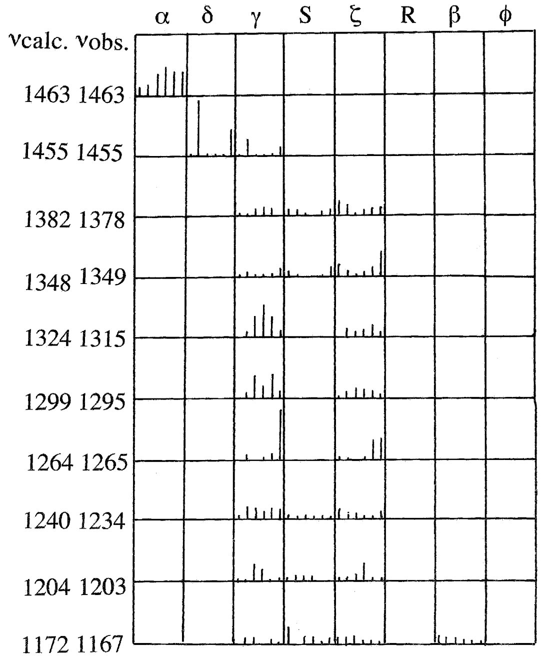

Fig. 6. Potential energy distribution based on the internal coordinates in the 1463–1167 cm^{-1} region. Each square contains six vertical lines corresponding to six monomer units (see text for detail).

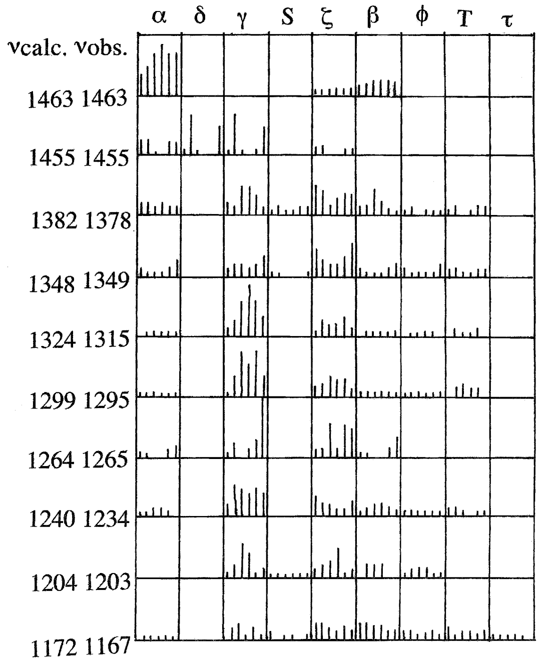

Fig. 8. **L** vector based on the internal coordinates in the 1463–1167 cm^{-1} region.

earlier. Major conformational sensitive bands are assigned to γ (CCH bend of CH_2). Since this mode is likely to be affected by the off-diagonal **F** matrix elements of adjacent CCH bend, the mode is conformationally sensitive. The second major conformational sensitive bands are β (CCH bend of CH_3). Since this mode is related to molecular packing, crystal structural change affects this mode.

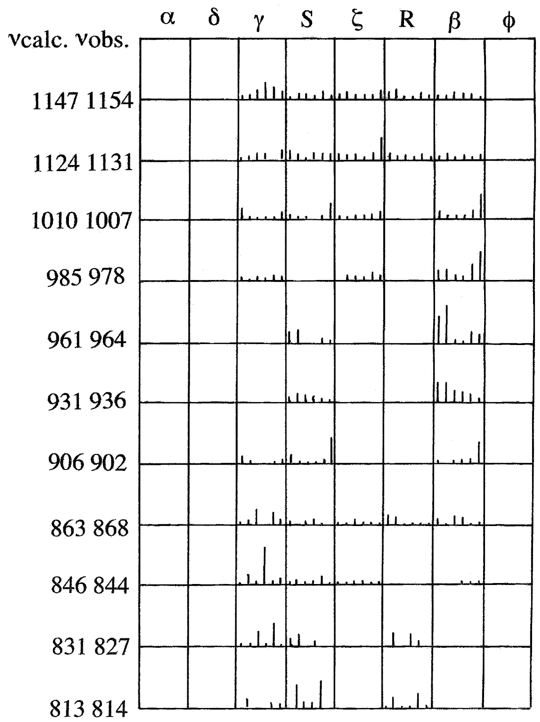

Fig. 7. Potential energy distribution based on the internal coordinates in the 1154–814 cm^{-1} region.

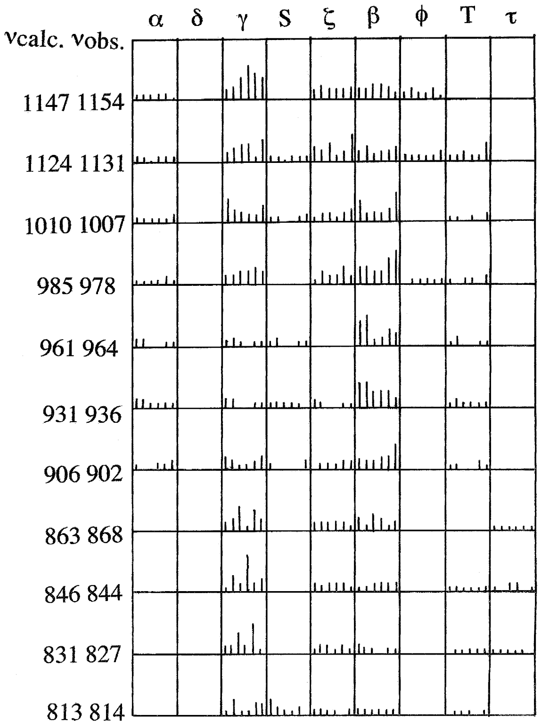

Fig. 9. **L** vector based on the internal coordinates in the 1154–814 cm^{-1} region.

Table 1
Observed (infrared) and calculated frequencies (cm^{-1}), and potential energy distribution (PED%) for syndiotactic polypropylene $T_2G_2T_6G_2$ form

$\nu_{\text{calc.}}$	$\nu_{\text{obs.}}$	PED[a]	Assignment[b]
2961	2964	r 99	r
2961	2956	r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2961		r 99	r
2931	2927	d 95	d
2929		d 95	d
2929		d 95	d
2929		d 97	d
2928		d 98	d
2927		d 99	d
2905		s 97	s
2903		s 97	s
2903		s 96	s
2903		s 96	s
2902		s 95	s
2901	2885	s 95	s
2882	2868	r 99	r
2882		r 99	r
2882		r 100	r
2882		r 99	r
2882		r 99	r
2882		r 99	r
2856		d 99	d
2856		d 99	d
2856		d 99	d
2855		d 99	d
2855		d 99	d
2854	2841	d 99	d
1469		α 74	α
1469		α 76	α
1468		α 79	α
1468		α 81	α
1467		α 84	α
1467		α 86	α
1466		α 75	α
1465		α 83	α
1465		α 86	α
1464		α 85	α
1464		α 86	α
1463	1463	α 88	α
1455	1455	δ 68, γ 20	δ
1454		δ 70, γ 21	δ
1453		δ 62, α 19, γ 14	δ
1452		δ 67, γ 19, α 12	δ
1451		δ 73, γ 20	δ
1438		δ 55, γ 27	γ
1408		γ 29, S 26, ζ 15	γ
1405		S 33, γ 29, ζ 22	γ
1401		γ 31, S 24, ζ 23	γ
1400		S 29, γ 29, ζ 25	S
1390		ζ 30, γ 23, S 21	ζ
1386		ζ 34, γ 24, R 15, S 11	ζ
1382		ζ 34, γ 21, S 20	ζ
1373	1378	β 23, α 21, ζ 21, R 15	β
1372		ζ 26, β 24, α 22, R 14	ζ
1371		β 46, α 38	β
1370		β 50, α 42	β
1369		β 49, α 41	β
1369		β 51, α 43	β
1367		β 36, α 31, ζ 15, γ 10	β
1365		ζ 28, β 23, α 21, γ 13	ζ
1364		ζ 48, γ 16, S 11	ζ
1358		ζ 44, γ 13, S 10	ζ
1348	1349	ζ 45, S 14, γ 13	ζ
1324	1315	γ 68, ζ 21	ζ
1299	1295	γ 62, ζ 26	γ
1271		γ 54, ζ 28	γ
1264	1265	γ 48, ζ 36	γ
1261		γ 48, ζ 37	γ
1240	1233	γ 46, ζ 24, S 10	γ
1225		ζ 29, γ 25, S 24	ζ
1219		ζ 31, γ 27, S 17	ζ
1208		ζ 39, γ 31, β 11	ζ
1204	1203	γ 27, ζ 25, S 17	γ
1197		γ 31, S 22, ζ 16, β 11	γ
1191		ζ 30, γ 27, S 16	ζ
1186		S 32, γ 19, β 16, ζ 13, ϕ 11	S
1181		γ 29, β 18, S 16, ζ 16	γ
1174		S 23, ζ 20, β 18, γ 18, ϕ 10	S
1172	1167	S 28, β 20, ζ 19, γ 13, ϕ 10	S
1147	1154	γ 39, S 14, R 13, ζ 13, β 12	γ
1141		R 28, ζ 19, β 16, S 12, γ 12	R
1124	1131	ζ 27, S 23, γ 21, R 12, β 10	ζ
1109	1107	γ 27, S 21, R 20, ζ 20	γ
1102		R 27, γ 24, S 21, γ 18	R
1091		γ 25, S 22, ζ 21, R 19	γ
1065		γ 27, S 24, ζ 18, β 14, R 11	γ
1041		γ 33, β 19, ζ 17, R 14, S 11	γ
1029		γ 33, ζ 21, S 14, R 14, β 14	γ
1010		β 37, S 19, γ 19, ζ 10	β
1002		β 38, γ 22, ζ 16, S 11	β
985	978	β 54, ζ 14, γ 14	β
968		β 45, ζ 20, γ 16, R 11	β
961	964	β 66, S 24	β
956		β 68, S 23	β
952		β 60, S 25	β
947		β 62, S 24	β
942		β 42, γ 25, ζ 18	β
931	936	β 56, S 27	β
906	912	S 33, β 30, γ 13	S
892		β 41, γ 21, ζ 17	β
888		β 41, γ 22, ζ 16, S 10	β
879		γ 31, β 27, ζ 14, S 11, R 10	γ
863	868	γ 32, β 20, R 19, ζ 12, S 11	γ
846	847	γ 47, S 15, ζ 12, β 10	γ
838		R 26, γ 25, S 18, β 11	R
831	827	γ 36, R 20, S 19	γ
813	814	S 48, R 20, γ 17	S
800		R 32, γ 31, S 19	R
787		S 32, R 30, γ 18	S
675	675	γ 34, S 32, ϕ 11	γ
582	588	ω 38, ϕ 29, γ 12	ϕ
566		γ 33, ϕ 26, ζ 11	γ
536		ϕ 43, ω 23, γ 10	ϕ

(*continued on next page*)

Table 1 (*continued*)

$\nu_{calc.}$	$\nu_{obs.}$	PED[a]	Assignment[b]
522	490	ϕ 39, ω 24, γ 14	ϕ
468	472	ϕ 43, γ 14, R 13, ω 11	ϕ
454		ϕ 43, γ 17, ζ 12, ω 11	ϕ
420		ϕ 46, ζ 22, γ 20	ϕ
410		ϕ 48, ζ 23, γ 20	ϕ
408		ϕ 51, ζ 20, γ 16	ϕ
396		ϕ 65, ζ11, γ 11	ϕ
392		ϕ 61, ζ 17, γ 13	ϕ
367		ϕ 57, γ 13, ζ 11	ϕ
358		ϕ 62, γ 10	ϕ
330		ϕ 52, γ 22, S 10	ϕ
299		ϕ 51, S 26	ϕ
287		ϕ 70, S 13	ϕ
282		ϕ 65, S 20	ϕ
224		ϕ 57, γ 20, ω 12	ϕ
209		ϕ 47, ω 32, γ 10	ϕ
181		ϕ 51, S 23, ω 14	ϕ
173		ω 58, ϕ 31	ω
153		ϕ 34, ω 32, γ 18	ϕ
137		γ 44, ϕ 27, ζ 11, ω 11	γ
98		ϕ 41, ω 40	ϕ
78		ϕ 38, ω 34, γ 15	ϕ
65		T 96	T
65		T 94	T
65		T 97	T
64		T 98	T
64		T 93	T
64		T 95	T
41		ϕ 46, ω 35	ϕ
32		τ 98	τ
22		τ 97	τ
22		τ 97	τ
20		τ 97	τ
15		τ 98	τ
12		τ 99	τ
2		τ 98	τ

[a] The values below 5% were neglected.

[b] The symbols were defined as follows: r CH_3 stretch, d CH_2 stretch, s CH stretch, γ CH bend (CH_2), α HCH bend (CH_3), β CCH bend (CH_3), δ HCH bend (CH_2), ζ CH bend (CH), S CC stretch (main chain), R CC stretch (side chain), ϕ CCC bend (CH), ω CCC bend (CH_2), T torsion (C–CH_3), τ torsion (C–C).

In this study, we have investigated the spectral changes accompanied by the crystal structural change of syndiotactic polypropylene. As the crystal structure changes from the all-*trans* to the ($T_2G_2T_6G_2$), and to the $(T_2G_2)_2$ form, fraction of the *gauche* components increases. At the same time, conformation-sensitive bands, which are ascribed to be *gauche* structure, increase in intensity.

Table 2
Characteristic bands of three crystalline forms of syndiotactic polypropylene

All-*trans*, $\nu_{obs.}$ (cm^{-1})	New form			Helix, $\nu_{obs.}$
	$\nu_{obs.}$	Assignment		
1465	1463	–	α	1464
1455	1455	G	δ	1432
1381	1378	–	β	1378
	1349	G	ζ	1345
				1333
1322	1315	T	γ	1312
	1295	T, G	γ	1287
	1265	G	γ	1263
1233	1233	–	γ	1232
1200	1203	T	γ	1201
	1167	–	S	1167
1154	1154	–	γ	1153
1130	1131	–	ζ	1130
				1088
				1035
	1007	G	β	1077
977	978	G	β	978
963	964	G	β	962
	936	G	β	934
900	902	G	β	904
867	868	–	γ	868
	847	T	γ	
829	827	T	γ	
	814	G	S	812

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