with $\tau_a = 1 \times 10^{-3}$, $\tau_b = 1 \times 10^{2}$, $\sigma = 0.04$, and $M = 30$, and $M = 50$, where λ was determined as described in section 3.2. The results are shown in Figure 3a,b and are in good agreement with the true relaxation spectrum (Figure 1). Furthermore, the result is independent of the number of relaxation times M introduced.

Finally, we determined the relaxation spectrum of a narrow distribution polybutadiene melt with $\bar{M}_w = 5.78 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1.05$ using data from Berger.[16] The values for the storage modulus and the loss modulus listed in Table III refer to a temperature of 23 °C. With $\sigma = 0.04$, $M = 50$, $\tau_a = 1 \times 10^{-4}$, and $\tau_b = 1 \times 10^{0}$, we obtained the relaxation spectrum shown in Figure 4a. Figure 4b shows the resulting storage modulus and loss modulus, which is in good agreement with the measured values.

As expected, nearly all h_α's are positive. Furthermore, there can be identified two peaks in the relaxation spectrum at $\tau \approx 8 \times 10^{-4}$ and $\tau \approx 2 \times 10^{-2}$ s. For small τ_α ($\approx 1 \times 10^{-4}$) the corresponding h_α's tend toward 0, and for large τ_α ($\gtrsim 1 \times 10^{-1}$) the h_α's seem to be compatible with 0.

There remain questions concerning the resolution of the obtained relaxation spectrum. Furthermore, the dependence of the accuracy of the obtained values on the number N of measured values and on the range in which measured values for $G'(\omega)$ and $G''(\omega)$ are available should be studied in the future.

5. Conclusions

It has been shown, that the results for the relaxation spectrum using a naive linear regression method are not satisfactory at all. Pointing out the reason for this, we proposed a solution method for the determination of the relaxation spectrum based on classical Tikhonov regularization. The method was tested using simulated experimental data, and the results obtained were in good agreement with the known relaxation spectrum. The application to real experimental data always leads to plausible results.

Acknowledgment. We thank Dr. L. Wedgewood for his critical reading of the manuscript.

Registry No. Polybutadiene, 9003-17-2.

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Polymorphic Structures and Molecular Vibrations of Syndiotactic Polystyrene

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ABSTRACT: Two crystal modifications, α and β, of syndiotactic polystyrene (SPS) were found by means of vibrational spectroscopic and X-ray diffraction methods. It has been revealed that the α phase, crystallized from the melt or by annealing glassy samples, consists of molecules having the all-trans (TT) skeletal conformation and the β phase, crystallized from solutions or by holding glassy samples in an atmosphere of solvent vapor, consists of the TTGG skeletal conformation. The infrared bands characteristic of these specific conformations were observed and compared with those of isotactic polystyrene with TG conformation. The thermal crystallization from the glassy state and a solid-state phase transition from β to α phase were followed by the infrared spectral change and DSC thermogram. The TT form is found to be more stable than the TTGG form under ambient conditions.

Introduction

Isotactic polystyrene (abbreviated as IPS) is representative of stereoregular polymers. Since the first invention by Natta et al. in 1955,[1] many studies have been reported on the structure of IPS and related low molecular weight compounds in crystalline and noncrystalline states. It is now well-known that in the crystalline state the IPS molecule assumes a (3/1) helical form with a regular repetition of trans (T) and gauche (G) conformations of the skeletal C–C bonds.[2,3] Another skeletal conformation having a nearly extended form consisting of a repetition of nonstaggered trans C–C bonds (with the internal rota-

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tion angle twisted by about 20° from the perfectly staggered trans form) has been found in IPS gels.[4-7] Molecular vibrations of IPS having the regular TG conformation have been investigated by means of infrared[8-10] and Raman[11] spectroscopies as well as by normal modes of analysis.[12,13] The molecular structure of IPS in noncrystalline phases, such as in glass,[14] solution,[14,15] and gel,[16-18] has also been studied.

Preparation of syndiotactic polystyrene (abbreviated as SPS), the other counterpart of stereoregular polystyrene, has been eagerly awaited for a long time in order to elucidate the relationship between stereochemical configuration and various physical and chemical properties of stereoregular polymers. However, it was not successful until Ishihara et al. obtained quite recently a series of highly crystalline SPS samples by using a specific catalytic system.[19,20]

With these samples, we started a study on the molecular level structures of SPS in crystalline and noncrystalline states, the polymorphism, the phase transition behavior, the molecular vibrations, and so on. The results are to be compared with the cases of IPS and isotactic and syndiotactic polypropylene. In particular, syndiotactic polypropylene (abbreviated as SPP) crystallizes in two modifications which are different in the molecular conformation: one being the TTGG form[21,22] and the other the all-trans (TT) form.[23] The TTGG form is stable in ambient conditions and the TT form is obtained when the melt-quenched sample is highly stretched in iced water.[24] The presence of two stable conformers in the crystalline phase is inferred from the potential energy calculation.[25] In the case of SPS, Ishihara et al.[19] suggested first an all-trans (TT) planar structure, and thereafter the present authors reported that there existed another crystal modification which consisted of TTGG-type molecular conformation.[26,27] Independently, Immirzi et al. reported quite recently the presence of TTGG-formed crystal modification of SPS.[28,29] It is of importance to elucidate the conformational stability of the SPS molecule and compare it with the case of SPP. The present paper deals with the polymorphic structures of crystalline SPS investigated by X-ray diffraction, vibrational spectroscopy, and DSC methods. The vibrational spectral features characteristic of the two molecular conformations of SPS are summarized and compared with those of IPS.

Experimental Section

Samples. The SPS (powder) samples used were supplied from Idemitsu Petrochemical Co. Ltd. Their weight-averaged molecular weights were measured as 7×10^4, 16×10^4, 35×10^4, and 114×10^4. The syndiotacticity was evaluated as 96% or more by ^{13}C NMR. The melting points were in the range 260–270 °C. The powder samples were first dissolved in chloroform, and film specimens were cast from the solution. The cast films held between two polished metal plates were heated in a Wood's alloy bath kept at 270 °C and then quenched in iced water, giving noncrystalline glassy films.

According to the crystallization condition, two types of crystal modification were obtained.[27] We refer them to α and β forms as described in the following.

α-SPS. Unoriented films of α form were obtained by annealing the quenched glassy films at 200 °C for 30 min. When a quenched film was drawn about 5 times the original length in boiling water and then annealed in a fixed-end state at 200 °C for 30 min, a uniaxially oriented film of α form was obtained.

β-SPS. Film samples cast from a chloroform solution were dried by keeping them in an evacuated desiccator for several days, and thereafter they were put in boiling water for several hours in order to remove contaminating solvent. Thus, we obtain unoriented films of β form. These samples showed infrared spectrum typical of this particular crystalline phase as described below, and removal of solvent was checked by elimination of the absorptions due to the solvent. Uniaxially oriented films of the

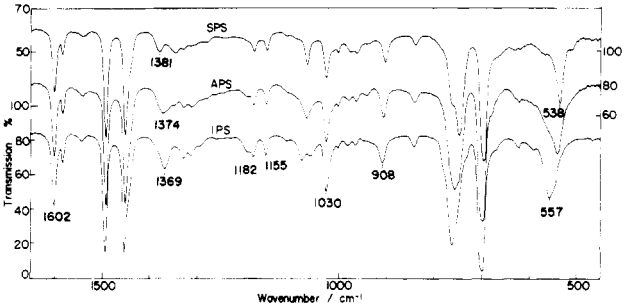

Figure 1. Infrared spectra of glassy films of syndiotactic, atactic, and isotactic polystyrene.

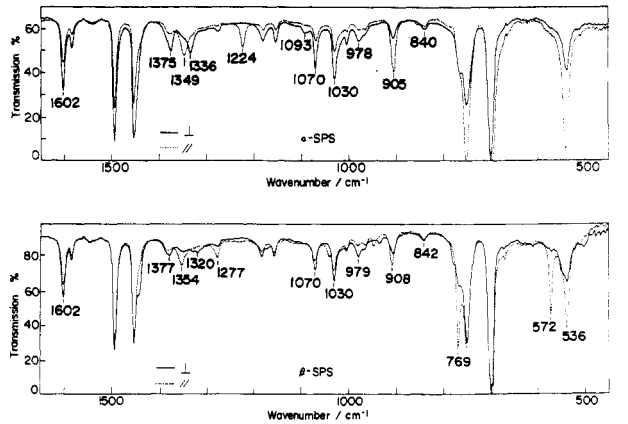

Figure 2. Polarized infrared spectra of uniaxially oriented films of α and β forms of syndiotactic polystyrene (SPS).

β form were prepared by holding stretched melt-quenched glassy films in a vapor of chloroform or benzene. The vapor exposure was continued until the infrared pattern was converted to that characteristic of the β form. The exposure time varied from a few days to a week depending on the film thickness. For thicker filaments used for the X-ray diffraction experiment, the oriented filaments (poorly crystallized in the α form) were immersed in benzene until the reflection due to the α form almost disappeared.

Isotactic and Atactic Samples. The IPS samples were obtained by polymerization with a Ziegler-type catalyst ($TiCl_3$–$(C_2H_5)_3Al$) in *n*-heptane at 70 °C. The unoriented and uniaxially oriented film specimens in the glassy and crystalline states were prepared through procedures similar to the case of α-SPS. The atactic polystyrene (APS) sample from a commercial source was used. Film specimens were cast from a benzene solution.

Spectral Measurements. Infrared spectra (with the 1-cm^{-1} resolution) were taken by using a JASCO 5MP and 8000 FT-IR spectrometer equipped with a DTGS detector. The number of accumulation cycles was in the range 50–100. Polarized spectra were measured with a wire-grid polarizer. The infrared spectra (in the region 1650–450 cm^{-1}) of SPS, APS, and IPS in the glassy state are reproduced in Figure 1. The polarized infrared spectra (1650–450 cm^{-1}) of uniaxially oriented films of α and β forms of SPS are reproduced in Figure 2. Here, the solid and broken curves represent, respectively, the absorption components polarized perpendicular and parallel to the fiber axis. The infrared spectra of the films prepared by exposure to different solvents were essentially the same, independent of the solvent used. Far-infrared spectra (with 2-cm^{-1} resolution) were taken by using a Perkin-Elmer 1800 FT-IR spectrometer equipped with a DTGS detector. The far-infrared spectra (500–150 cm^{-1}) of α- and β-SPS along with crystalline IPS are shown in Figure 3.

Raman spectra were taken with a JASCO R-500 double monochromator with the 514.5-nm excitation light from an Ar^+ laser. Raman spectra of α- and β-SPS are shown in Figure 4.

X-ray Diffraction. Fiber diffraction patterns of uniaxially oriented specimens of α and β forms of SPS were taken with a cylindrical camera of 57.3-mm diameter with the Cu Kα line monochromatized by a Ni filter. The photographs are shown in Figure 5.

DSC Measurement. Thermograms on the heating or cooling processes of various samples were taken by using a Seiko Model 20 DSC at the heating (or cooling) rate of 3 °C/min.

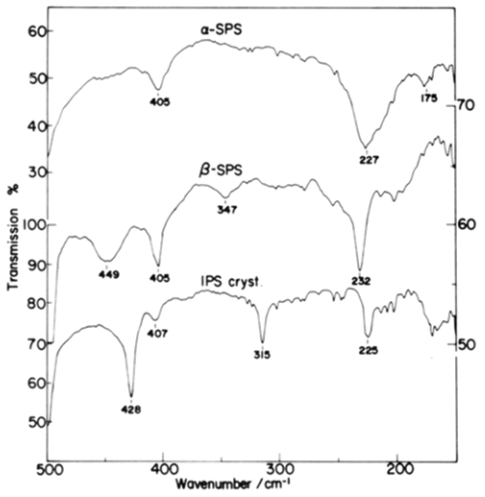

Figure 3. Far-infrared spectra of α-SPS, β-SPS, and isotactic polystyrene (crystalline).

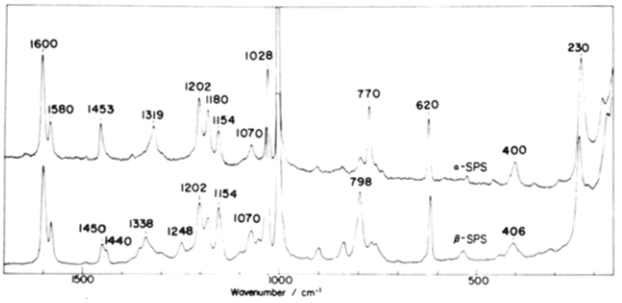

Figure 4. Raman spectra of α-SPS and β-SPS.

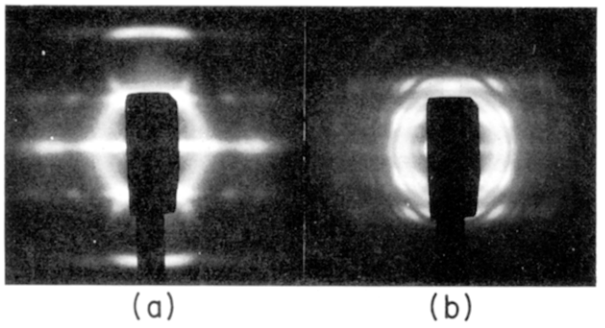

Figure 5. X-ray fiber photographs of (a) α-SPS and (b) β-SPS.

Results and Discussion

Molecular Structures of α and β Phases of SPS. The fiber identity periods of α and β phases were measured from the fiber diagram (Figure 5) as 0.5 and 0.75 nm, respectively. This suggests, by analogy with the case of SPP, that the α phase takes an all-trans planar zigzag (TT) skeletal conformation and the β phase a TTGG-type conformation presumably forming a twofold helical structure, as depicted in Figure 6.

Although the twofold helical conformation of the β form has not been confirmed by the X-ray diffraction, the polarized infrared spectra were well interpreted by the normal-mode analysis made on a molecular model having D_2 symmetry. Immirzi et al.[28] proposed that SPS films treated with solvents formed solvent-complexed structures. The X-ray fiber diagram of the present sample (Figure 5b) corresponds to a superposition of those of the methylene chloride complex (sample 2) and dried film (sample 5) reported in ref 28 and summarized in Table I. This indicates that the present sample (treated with benzene as described in the preceding section) contains benzene-complexed structure in addition to the dried β-SPS structure. Formation of such a solvent complex is suggested also from the polarized infrared spectra of oriented

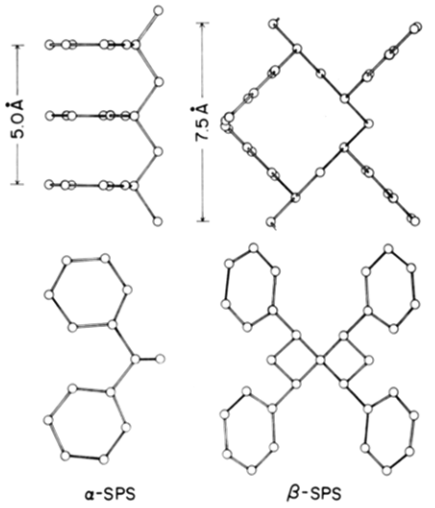

Figure 6. Schematic representation of molecular structures of α-SPS and β-SPS.

Table I
Diffraction Angles (in deg; Cu Kα Radiation) and Relative Intensities in Fiber Diagrams of β-SPS Samples

present sample[a]	sample 2[b]	sample 5[c]
	Equator	
7.8 m	8.2 s	
9.2 m		9.3 s
10.3 s	10.3 m	10.4 s
17.5 w	16.1 m	15.7 m
		19.0 ms
20.7 m	20.6 w	21.0 m
23.3 m		23.0 w
	First Layer	
12.5 m	13.3 s	
16.8 vs	17.3 s	16.1 vs
20.5 vs	20.8 vs	19.9 s
	23.6 m	23.9 m
26.2 w		

[a] A filament treated with benzene and, thereafter, held in boiling water for removal of the contaminating solvent (see text). [b] SPS–methylene chloride complex reported in ref 28. [c] SPS treated with methylene chloride and then annealed at 120 °C for 2 h (ref 28).

Table II
Number of Normal Modes and Selection Rules for α-SPS, β-SPS, and IPS Molecules[a]

species	n_i	T, R	infrared	Raman
		α-SPS (TT; C_{2v})		
A_1	29	T_x	A(⊥)	A
A_2	17		F	A
B_1	29	T_y, R_z	A(⊥)	A
B_2	17	T_z	A(∥)	A
		β-SPS (TTGG; D_2)		
A	47		F	A
B_1	47	T_x	A(⊥)	A
B_2	47	T_y	A(⊥)	A
B_3	47	T_z, R_z	A(∥)	A
		IPS (TG; C_3)		
A	46	T_z, R_z	A(∥)	A
E	47 × 2	(T_x, T_y)	A(⊥)	A

[a] A, active; F, forbidden; T, pure translation; R, pure rotation around the chain axis; x parallel to the chain axis; y and z, perpendicular to the chain axis.

β-SPS films immersed in benzene. The bands associated with the contaminating benzene molecules exhibit clear polarization.

The molecular conformations of the two crystalline phases of SPS derived from the X-ray fiber patterns are supported by the infrared and Raman spectral features. The number of normal modes and the infrared and Raman selection rules of the symmetry species of the (TT) and (TTGG) molecules of SPS are summarized in Table II, in

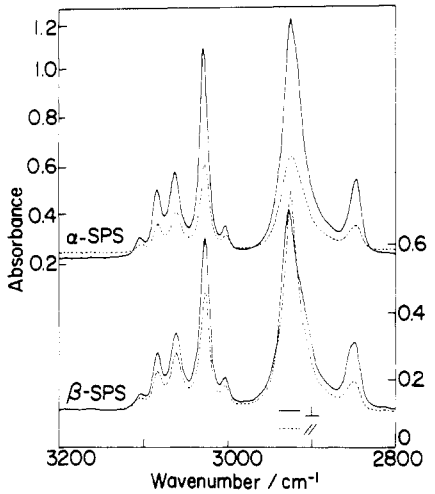

Figure 7. Polarized infrared spectra (in the C–H stretch region) of uniaxially oriented films of α-SPS and β-SPS.

comparison with the case of the threefold helical (TG) molecule of IPS. Here, we assume that in the TT-formed SPS molecule the plane of the phenyl ring is located perpendicular to the zigzag skeletal plane (having the C_{2v} factor group symmetry) and that the TTGG molecule has the twofold screw axis along the chain axis and two twofold rotation axes that pass through the methylene carbon atoms and cross perpendicularly the twofold screw axis (the D_2 factor group symmetry).

Table II tells us the following things:

1. The number of infrared bands of the TT-SPS molecule is far smaller than that of the TTGG-SPS or the TG-IPS molecule, because of the difference in the number of monomeric units contained in the fiber period, as well as in the factor group symmetry (TT-SPS, two units with C_{2v} symmetry; TTGG-SPS, four units with D_2 symmetry; TG-IPS, three units with C_3 symmetry). The difference in the number of detected infrared-active bands between the two modifications of SPS is quite obvious in the region 1100–500 cm^{-1} (see Figure 2). The number of Raman-active bands is, however, not so different between the two (Figure 4) as infrared bands, because most of the Raman bands observed are due to the ring modes, which are scarcely separated by the symmetry species.

2. The difference in molecular conformation is reflected in the infrared polarization of the ring modes. In the TTGG-SPS molecule, one ring mode splits into four different symmetry species, three of which are infrared-active. However, for most of the ring modes, the spectral components due to different species are located very close to each other and, hence, actually overlap at the same frequency because of comparatively weak intrachain coupling between neighboring phenyl rings. Therefore, the parallel (B_3) and perpendicular (B_1 and B_2) infrared-active components of a particular ring mode overlap each other, resulting in a dichroic ratio determined by the orientation of the local transition dipole of the mode with respect to the fiber axis. In case of ring C–H stretch modes, the dichroic ratios are expected to be close to unity since the phenyl rings are inclined to the fiber axis by about 45°. On the contrary, in the TT-SPS molecule the out-of-plane ring modes belong to B_2 (with IR polarization parallel to the fiber axis), and the in-plane ring modes belong to A_1 or B_1 (with IR polarization perpendicular to the fiber axis). Therefore, all the ring modes might exhibit well-defined polarization. The observed infrared bands due to the ring C–H stretch modes (the in-plane modes) and the skeletal C–H stretch modes as well, of the α form, exhibit clear perpendicular polarization, compared with those of the β form (Figure 7). This also supports our conclusion about the molecular conformation of the two modifications of SPS.

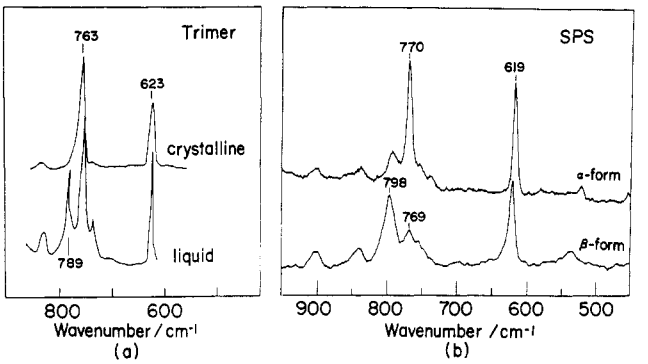

Figure 8. Comparison of Raman spectra of (a) racemo-racemo 2,4,6-triphenylheptane[7] and (b) two crystal modifications of SPS.

Table III
Conformational-Sensitive Infrared Bands of Syndiotactic and Isotactic Polystyrenes (cm^{-1})

α-SPS (TT)	β-SPS (TTGG)	IPS (TG)	assignments[b]
1375(⊥) m[a]	1377(⊥) w[a]	1365(⊥) m[a]	δ(CH), w(CH_2)
1349(∥) m	1354(∥) m	1327(∥) w	S, w(CH_2), δ(CH)
1336(⊥) m	1320(⊥) w	1315(⊥) w	w(CH_2), δ(CH)
1224(∥) m	1277(∥) m	1197(∥) s	S, δ(CH)
1070(⊥) m	1070(⊥) m	1083(⊥) s	S, ring(i)
		1053(⊥) m	
905(∥)	908(∥, ⊥)	923(⊥) m	$\gamma(CH)_r$, ring(o)
		899(∥) m	$\gamma(CH)_r$, r(CH_2)
	769(∥) vs	783(∥)	S, ring(i)
751(∥) vs	750(∥) vs	764(∥) vs	$\gamma(CH)_r$
		620(∥) m	ring(i)
	572(∥) vs	580(∥) vs	ring(i), $\beta(CH)_r$
537(∥) vs	536(∥) vs	566(∥) vs	S, ring(o), $\gamma(CH)_r$

[a] Relative intensities: w, weak; m, medium; s, strong; vs, very strong. [b] δ(CH), methine CH deformation, w(CH_2), methylene wagging; r(CH_2), methylene rocking; $\beta(CH)_r$, ring CH in-plane deformation; $\gamma(CH)_r$, ring CH out-of-plane deformation; S, skeletal mode; ring(i), in-plane ring mode; ring(o), out-of-plane ring mode.

As for the relationship between vibrational spectra and molecular conformation of SPS, Jasse et al.[11] investigated Raman spectra of the racemo-racemo-type stereoisomer of 2,4,6-triphenylheptane (a trimer of SPS). This compound gives rise to two bands at 763 and 623 cm^{-1} in a crystalline state, while in a liquid state additional bands appear at 789 and 737 cm^{-1} (Figure 8a), indicating that there are at least two conformers in the liquid state. If we compare the Raman spectra of α- and β-SPS in the same region (Figure 8b with Figure 8a), it is evident that the crystalline trimer and the α-form take the same TTTT conformation. This is consistent with the fact that the most stable conformation of the syndiotactic dimers and trimers so far investigated is the all-trans form. The 789-cm^{-1} band of the liquid trimer corresponds to the 798-cm^{-1} band of β-SPS, indicating that the additional conformer present in the liquid state contains gauche C–C bonds like in β-SPS.

Conformational-Sensitive Bands of SPS. In previous works on molecular vibrations of polystyrene, it has been revealed that most of the infrared and Raman bands characteristic of IPS are due to some specific intramolecular interactions in regular sequences of the TG skeletal conformation. These bands appear in highly crystalline states as well as in CS_2 solution cooled at a low temperature.[9,15] In the case of SPS, the corresponding bands characteristic of the TT or TTGG conformation are found in the spectra of α- or β-SPS by comparing them with the spectra of glassy SPS. They are used as the key bands for the identification of crystal modification or of particular local conformation present in noncrystalline phases. The frequencies and the polarizations of the conformational-sensitive infrared bands of the TT and TTGG forms of

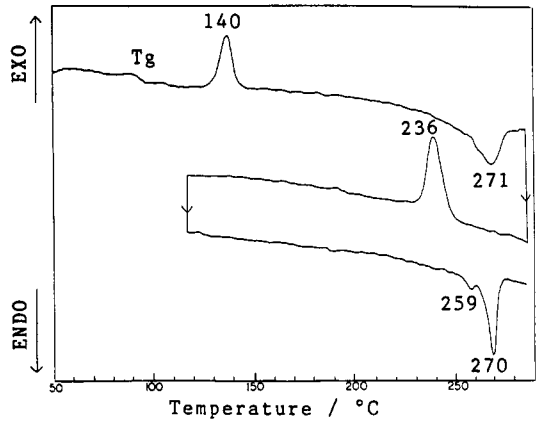

Figure 9. DSC thermogram on a crystallization process of SPS from a glassy state.

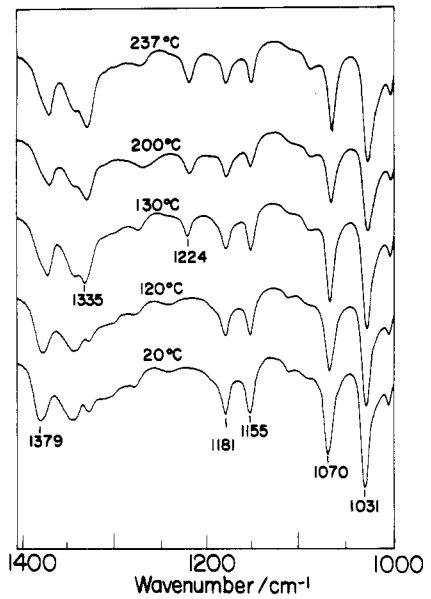

Figure 10. infrared spectral change on a heating process of a glassy film of SPS. Appearance of the 1335- and 1224-cm^{-1} bands above 130 °C indicates that the resultant crystalline phase is α.

SPS along with those of the TG form of IPS are listed in Table III. The assignments of the bands given here were made on the basis of normal-modes calculation, the detail of which will be reported elsewhere.

Crystallization and Solid-State Phase Transition. As a glassy film of SPS is heated, it begins to crystallize at about 140 °C with an exotherm of about 14 J/g and, then, melts at about 270 °C with an endotherm of 28 J/g as shown in the DSC thermogram (Figure 9). During this heating process, the infrared spectrum changes as shown in Figure 10. The appearance of the 1335- and 1224-cm^{-1} bands on crystallization indicates that the resultant crystalline phase is the α modification. The temperature T_c at which the crystallization starts and the magnitude of the accompanying exotherm varied somewhat depending on the molecular weight as well as on the heating conditions.

As a β-SPS film is heated, it transforms to the α modification at about 180 °C as followed by the infrared spectral change shown in Figure 11. The transformation is clearly detected by the appearance of the 1224-cm^{-1} band (α) and the disappearance of the 935-cm^{-1} band (β). In the DSC thermogram, we could detect a weak exotherm peak at 180 °C, although it was too weak to evaluate its magnitude. Thus, in the dried state, the α phase consisting of the all-trans skeletal conformation is thermodynamically more stable than the β phase consisting of the TTGG conformation. In the construction of the TTGG conformation, presence of solvent seems to take an essential part. The reverse is true in syndiotactic polypropylene (SPP), where the TTGG form is always obtained through the ordinary crystallization process from the melt or from solution, while the TT form is obtained by stretching a melt-quenched sample in iced water. The difference in the conformational stability between SPS and SPP may be ascribed to the difference in the shape and bulkiness of the pendant group.

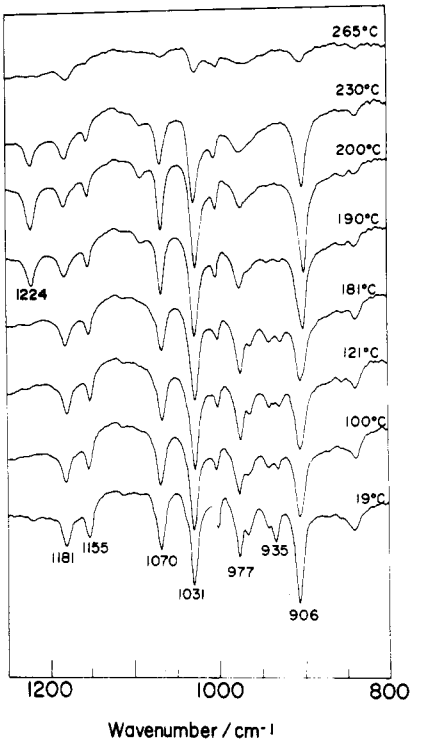

Figure 11. Infrared spectral change on a heating process of β-SPS. Appearance of the 1224-cm^{-1} band and disappearance of the 935-cm^{-1} band above 190 °C indicates that β transforms to α.

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Notes

Carboxylic Acid, Ester, and Lithium Carboxylate Derivatives of Poly(methylphenylphosphazene)

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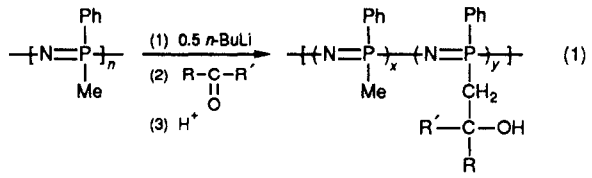
Introduction

Polyphosphazenes, $[R_2PN]_n$, are an unusual class of polymers in that the properties of this system can be varied over a very wide range through the incorporation of different substituents on the phosphorus. While literally hundreds[1] of polyphosphazenes with alkoxy, aryloxy, and amino groups have been prepared, phosphazene polymers with all substituents attached to the backbone by direct P–C bonds are relatively new and few in number.[2] As part of our ongoing studies of this type of phosphazene, i.e., the poly(alkylarylphosphazenes), we are investigating methods of diversifying the functional groups R on phosphorus. We have found that the deprotonation of methyl substituents on preformed poly(methylphenylphosphazene), $[Ph(Me)P{=}N]_n$, followed by reaction of the resulting ion with various electrophiles, provides access to P–C-substituted polymers with reactive functional groups.[3-5] For example, we recently reported the use of this deprotonation–substitution process to prepare a series of polyphosphazenes with alcohol substituents attached to the phosphorus through a CH_2 spacer group (eq 1).[4,5] We have also prepared graft copolymers by using the intermediate anion for the initiation of addition polymerization of styrene and for the ring opening of hexamethylcyclotrisiloxane.[6,7]



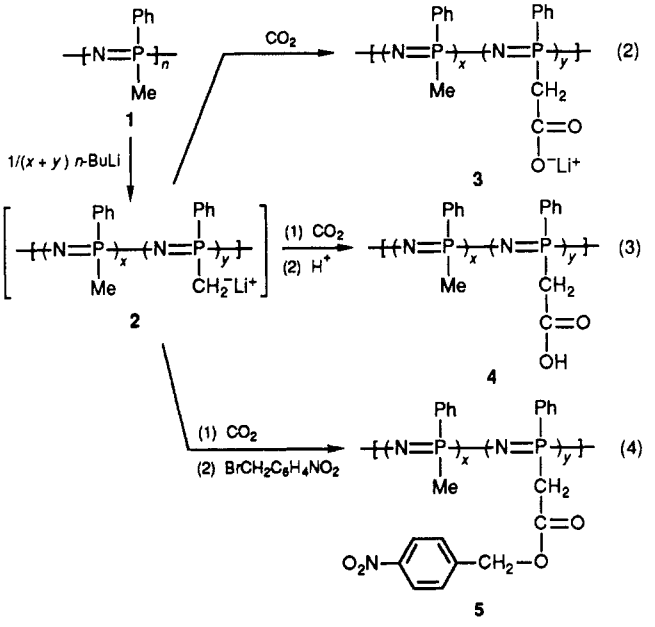
(1)

In this paper we report the use of the deprotonation–substitution process for the preparation of polyphosphazenes with carboxylate, carboxylic acid, and ester functional groups. The synthesis, characterization, and simple properties of these new phosphazenes, one of which is the first water-soluble P–C-substituted polyphosphazene, are discussed.

Results and Discussion

A series of carboxylated derivatives of $[Me(Ph)PN]_n$ in which 10, 25, and 50% of the PN monomer units contained either $CH_2COO^-Li^+$, CH_2COOH, or $CH_2COOCH_2C_6H_4$-4-NO_2 groups was prepared by initial formation of the anionic polymer intermediate by deprotonation of the appropriate number of PMe groups in the parent polymer with *n*-BuLi. Treatment of the viscous THF solution of the polymer anions **2** at −78 °C with anhydrous, gaseous carbon dioxide produced the THF-insoluble carboxylate salts, **3a–c** (eq 2; Scheme I), which could be isolated by simple removal of the solvents. Treatment of these salt slurries with aqueous solutions of HCl or with *p*-nitrobenzyl bromide resulted in the acid and ester derivatives **4a–c** and **5a–c**, respectively (eq 3 and 4; Scheme I).

Scheme I[a]



[a] **a**: $x = 9, y = 1$. **b**: $x = 3, y = 1$. **c**: $x = 1, y = 1$.

The salt derivatives **3a** and **3b** were insoluble in THF, hydrocarbons, and water but soluble in 1:1 mixtures of THF and water. Polymer **3c**, on the other hand, was quite water soluble and insoluble in organic solvents. All of the salts, **3a–c** formed extremely viscous gels in chlorinated hydrocarbons, which facilitated their characterization by NMR spectroscopy. The acid derivatives, **4a–c**, and the esters, **5a–c**, were soluble in THF and chlorinated hydrocarbons, and polymer **4c** showed some tendency to dissolve in H_2O. The new polymers were off-white ma-

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