identical primary structures (amino acid sequence).

We consider the relation between the anisotropic ^{15}N chemical shift tensors and the conformation of copolypeptides below. It is obvious that σ_{11} and σ_{22} depend on the conformation of the polypeptides in the solid state, whereas the dependency of σ_{33} on conformation is not clear here. We emphasize that the σ_{22} values of the Ala* of the α-helix and β-sheet forms are observed separately in the ranges 54–59 and 61–63 ppm, respectively. Moreover, since the experimental error of the σ_{22} value is very small, it is emphasized that the chemical shift displacement of this peak (σ_{22}) is very useful for conformational analysis of solid copolypeptides (or probably of some proteins), if the ^{15}N-labeled copolypeptide (or protein) can be provided.

On the other hand, it is interesting to note that the chemical shift displacement of σ_{11} in the copolypeptides is unique. That is to say, σ_{11} of Ala* of the α-helix (204–208 ppm) is displaced downfield in comparison with that of the β-sheet form (200–202 ppm). Since it has been determined that the downfield tensor element σ_{11} of dipeptide is nearly parallel to the hydrogen bonding (N–H···O) direction,[19–21] σ_{11} is considered to be useful for the study on the manner of the hydrogen bonding of polypeptides and proteins.

Registry No. Ala (homopolymer), 92537-95-6; Ala (SRU), 92538-24-4; [Ala*,Leu]$_n$, 81372-96-5; [Ala*,Asp(OBzl)]$_n$, 120497-46-3; [Ala*,Glu(OBzl)]$_n$, 120497-47-4; [Ala*,Glu(OMe)]$_n$, 81372-95-4; [Ala*,Val]$_n$, 81372-91-0; [Ala*,Ile]$_n$, 120497-48-5; Ala* NCA, 120575-41-9; Leu NCA, 3190-70-3; Asp(OBzl) NCA, 13590-42-6; Glu(OBzl) NCA, 13590-42-6; Glu(OMe) NCA, 1663-47-4; Val NCA, 24601-74-9; Ile NCA, 45895-90-7.

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Raman Spectroscopic Characterization and Molecular Force Field Development of a Synthetic Polyamide: Nylon 66

Molecular force fields may be determined from an analysis of vibrational spectra. A very limited set of macromolecular force fields have been determined by three distinctly different approaches. Often the only approach possible has been the overlay method,[1] by which a self-consistent force field is refined from the spectral data of the polymer and model small molecules. This method has been applied to a broad range of polymers but is not completely satisfactory when the molecules used to construct the overlay are not isostructural. This procedure has been used most successfully for a series of matrix-isolated *n*-alkanes[2] at low temperature with subsequent extension to polyethylene. Relevant to the present study, Jakes and Krimm[3] developed a force field from the infrared spectra of seven nylons, five N-deuterated analogues, and eight deuterated isotopomers of *N*-methylacetamide. This force field was then successfully used to calculate, without modification, the vibrational spectra of three other nylons and several *N*-alkyl amides and diamides.[4] Ab initio methods have also been used for both small and polymeric molecules to construct molecular force fields. This method is quite satisfactory for developing a force field when the system is sufficiently small to be tractable. In polymeric systems, because of the very large number of atoms that must be considered, this approach is difficult; however, some success has been achieved both for well-ordered systems[5] and for highly disordered polymers[6] through density-of-states calculations. A third approach, the isotopic substitution method, involves the use of a single polymer and specifically labeled isotopomers. This method is the most rigorous and provides for the correct assignment of the observed vibrational bands to the various normal modes. Unfortunately, this method is limited by the availability of isotopomers which are of sufficiently high isotopic purity. Because of the high cost and intense synthetic effort necessary, the force fields of only a few selected polymers have been developed by this method: polyethylene,[7,8] poly(alkylethylenes),[9,10] polypropylene,[11] poly(methyl methacrylate),[12] polyglycine,[13,14] and poly(ethylene terephthalate).[15]

Synthetic polyamides are closely related in structure to polypeptides and proteins and, as a class, are excellent model compounds for these important biological species. While the crystal structure of polyamides has been extensively characterized by X-ray diffraction,[16–20] it is only

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recently that detailed studies of their molecular dynamics have been undertaken.[21] As part of that effort, the goals of the work reported in this paper are to develop a molecular force field for nylon 66 (poly(hexamethyleneadipamide)) that could (1) serve as a basis set in the calculation of normal coordinates for similar polymers, especially peptides and proteins, and (2) be used to refine molecular dynamics calculations.

We have chosen to characterize the vibrational spectrum of nylon 66 with Raman spectroscopy because this method is nondestructive and does not require any modification of the physical form of the polymer; thus we are able to directly compare these results to those obtained with other techniques for polymers of identical history and morphology. In contrast, infrared spectroscopy, which has been used extensively in the past to characterize nylons,[3,19,22-31] would require casting the fibrous polymers into a film, which would change the morphology and possibly scramble the labile deuterons. Alternatively, infrared measurements could be made by diffuse reflectance infrared spectroscopy; however, vibrational band intensities obtained with this method often do not accurately reflect the population of the various chemical moieties. Previous Raman measurements of nylons have been very limited.[32,33] These spectra have exhibited a large fluorescent background, which has restricted the signal-to-noise quality of the data, hampering analysis. The high level of fluorescence in these previously obtained spectra, which were obtained with visible excitation, is presumably due to the presence of small concentrations of adventitious impurities and/or additives, such as UV stabilizers. In light of these previous results, we expected that the labeled polymers that we have synthesized (vide infra) for this study could not be characterized by conventional visible Raman spectroscopy and that FT Raman spectroscopy[34,35] would have to be used to avoid fluorescence. However, all the labeled polymers have exhibited low levels of fluorescence when irradiated in the visible, thus allowing Raman spectra to be measured on a conventional scanning spectrometer.

Six isotopically labeled nylon 66 polymers were prepared[36] by low-temperature interfacial polymerization of either the labeled hexamethylenediamine or the adipoyl chloride with the unlabeled counterpart. Five polymers were selectively deuterated at symmetrical pairs of methylene groups, which were α, β, or γ to the nitrogen in the diamine moiety or α or β to the carbonyl in the adipoyl moiety. The sixth polymer was ^{13}C labeled at the carbonyl group. The as-polymerized materials are designated by the following nomenclature (labeled monomer): NY16NH (hexamethylene-*1,1,6,6*-d_4-diamine), NY25NH (hexamethylene-*2,2,5,5*-d_6-diamine), NY34NH (hexamethylene-*3,3,4,4*-d_4-diamine), NY25CO (adipoyl-*2,2,5,5*-d_4 chloride), and NY34CO (adipoyl-*3,3,4,4*-d_4 chloride). The fully protonated and unlabeled polymer, designated as the control, was synthesized with the same thermal and solution processing history, ensuring the same molecular weight distribution and morphology as the labeled polymers. Previous characterization studies[36] have shown that except for the presence of a 6–14% low molecular weight component, the as-polymerized materials have molecular weights and molecular weight distributions that are quite similar to a reference commercial nylon. The as-polymerized materials possess only the α crystalline modification and have been determined to be approximately 35% crystalline by X-ray diffraction.

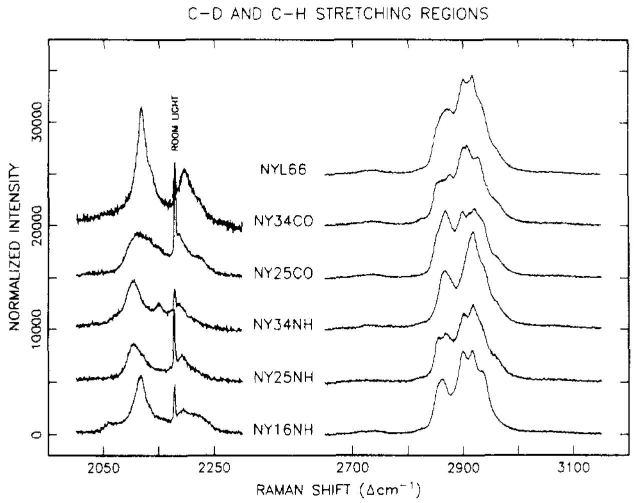

Figure 1. Normalized Raman spectra of nylon 66 and five deuterated isotopomers in the C–H and C–D stretching region. The top spectrum, NYL66, is of the fully protonated control nylon. The three lower spectra are of the polymers that are specifically deuterated at the methylene groups α (NY16NH), β (NY25NH), and γ (NY34NH) to the amide in the hexamethylenediamine moiety. The remaining two spectra are of the polymers that are deuterated at the methylene groups α (NY25CO) and β (NY34CO) to the amide group in the adipoyl moiety.

Table I
Vibrational Band Frequencies and Assignments in the C–H and C–D Stretching Regions

CH band: Δ, cm^{-1}	CD band: Δ, cm^{-1}	isotopic ratio	methylene species	tentative assignment
2738 ± 6			β-NH	
	2060		α-NH	
2822 ± 3	2114	1.33	α-CO	ν_s
2853 ± 3	2104	1.36	γ-NH	ν_s
2862 ± 1	2105	1.36	β-NH	ν_s
2868 ± 1	2119	1.35	β-CO	ν_s
2875 ± 2	2116	1.36	α-NH	ν_s
	2121 (sh)		β-NH	
	2135 (sh)		β-CO	
2899 ± 1	2147	1.35	γ-NH	ν_{as}
	2150 (sh)		α-CO	
2905 ± 1	2185	1.33	β-CO	ν_{as}
	2185		γ-NH	
2918 ± 2	2197	1.33	α-CO	ν_{as}
2932 ± 4	2192	1.34	β-NH	ν_{as}
	2215		α-NH	
	2221 (sh)		β-CO	
2954	2223	1.33	α-CO	
2960 ± 2	2193	1.35	α-NH	ν_{as}

Raman spectra were recorded, at 4-cm^{-1} spectral resolution by illuminating the fibrous powder with a few hundred milliwatts of 488-nm laser light. Since the N–H stretch at 3300 cm^{-1} of the hydrogen-bonded amide is isolated from other molecular vibrations, the integrated intensity of this band was used to normalize the intensities of the individual spectra. There was no evidence of any band at 3450 cm^{-1}, indicating the absence of any significant amount of free N–H. In addition, a band at 2180 cm^{-1} arising from the fluorescent room lights was used to verify the absolute frequency of the measured Raman shifts.

Figure 1 illustrates that the C–H stretching region of the Raman spectrum of the unlabeled control polymer (NYL66) is quite complicated, having many bands which are highly overlapped. Examination of the spectra of the specifically deuterated polymers reveals, in each case, a number of bands that shift from the C–H stretching region to the C–D stretching region. Correlating the bands that disappear in the C–H stretching region and reappear in the C–D stretching region with the site of deuteration allows assignment of those bands that arise from the five different pairs of methylene groups as shown in Table I.

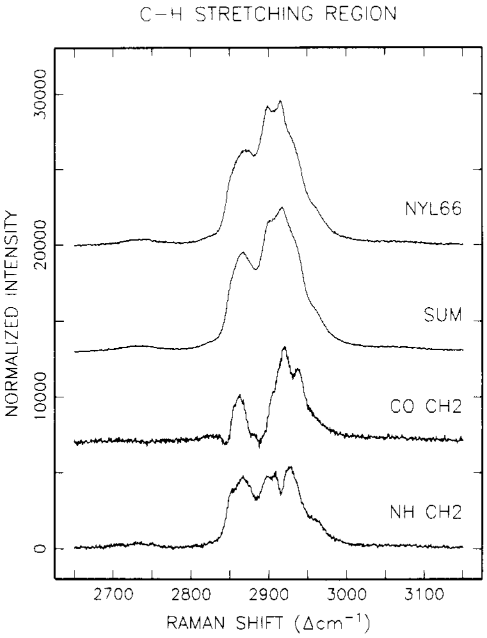

Figure 2. Digitally manipulated spectra of nylon 66 in the C–H stretching region. The upper spectrum, NYL66, is the measured Raman spectrum of the control polymer. The spectrum, SUM, is a normalized summation of the spectra of the five deuterated isotopomers. The lower two spectra, CO CH_2 and NH CH_2, reflect the contributions to the C–H stretching region of the methylene groups in the adipoyl and hexamethylenediamine moieties, respectively (see text).

By simple inspection, we have been able to establish the molecular origin, i.e., the specific methylene group, of all bands observed in the C–H and C–D stretching regions. Additionally, 11 of the 12 observed C–H bands have been mapped to a corresponding C–D band by using isotopic ratios of 1.33 to 1.36, in good agreement with the experimental infrared work done by Heidemann and Zahn[38] on films of NY16NH and NY25CO and the theoretical work by Krimm.[37] In both the C–H and C–D stretching regions, 10 fundamental bands are expected: a symmetric stretching band and an antisymmetric stretching band from each of the five chemically distinct methylene groups. Of the two additional bands observed in the C–H region, the band at 2954 cm^{-1} may be due to Fermi resonance.[39,40] The other band at 2738 cm^{-1} is an overtone or combination band, which is also found in the spectra of a variety of molecules containing *n*-alkane moieties: semifluorinated *n*-alkanes,[41] poly(alkylethylenes),[9,10] and phospholipids.[42] The molecular motions giving rise to this band are unknown, but some indication of their nature might be gleaned from the absence of this band when the β-NH methylene is deuterated. Of the 18 bands observed in the C–D stretching region, seven have not been mapped to a corresponding feature in the C–H region. Four of these seven bands are weak shoulders,[43] making any correlation to the heavily congested C–H region very difficult. A thorough band deconvolution of the C–H stretching region may provide bands that correspond to the three remaining C–D bands.

Digital manipulation of the spectra provides insight into the vibronic coupling and surprisingly the molecular dynamics of the methylene segments. Summation of the spectra of the five deuterated nylons yields a synthetic spectrum (SUM) which has contributions from each pair of methylenes:

$$\mathrm{SUM} = \tfrac{1}{4}(\mathrm{NY16NH} + \mathrm{NY25NH} + \mathrm{NY34NH} + \mathrm{NY25CO} + \mathrm{NY34CO})$$

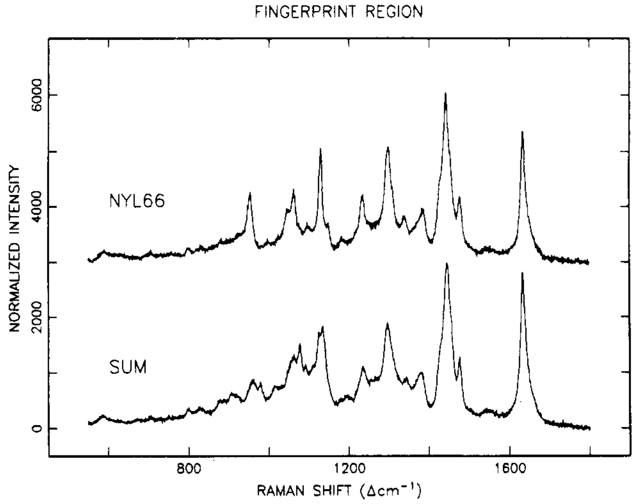

Figure 3. Raman spectra of nylon 66 in the fingerprint region, 500–1800 cm^{-1}. The upper spectrum, NYL66, is the measured Raman spectrum of the control polymer. The lower spectrum, SUM, results from the normalized summation of the spectra of the five deuterated isotopomers.

Comparison of the SUM spectrum with that of NYL66 in Figure 2 shows excellent agreement, indicating that deuteration of a methylene pair has only a small effect on the intensity and position of the vibrational bands that arise from the other four methylene pairs. This result supports the view that the individual normal modes of the C–H stretches are, in general, highly localized and are not substantially coupled with other molecular motions.[44] This conclusion is further supported by the two lower spectra in Figure 2, which were obtained by the following spectral manipulations:

$$\mathrm{NH\,CH_2} = \mathrm{NY25CO} + \mathrm{NY34CO} - \mathrm{NYL66}$$

$$\mathrm{CO\,CH_2} = \mathrm{NY16NH} + \mathrm{NY25NH} + \mathrm{NY34NH} - 2(\mathrm{NYL66})$$

These spectra should have contributions from all of the CH_2's in the hexamethylene (NH CH_2) and adipoyl moieties (CO CH_2), respectively. The individual features in these two spectra correspond within 5 cm^{-1} of the corresponding bands (listed in Table I) observed for the unlabeled polymer and clearly show which features are due to the methylene groups in the hexamethylene and adipoyl moieties, respectively.

The fingerprint region of the Raman spectrum of the unlabeled control polymer, NYL66, is shown in Figure 3. In this region (500–1800 cm^{-1}), the amide I and amide II bands at 1664 and 1545 cm^{-1}, respectively, are clearly observed. Comparison of the spectra of the control and ^{13}C-labeled nylons illustrates that the bands at 1232-, 1339-, and 1385-cm^{-1} shift to 1227, 1332, and 1379 cm^{-1}, respectively. It is likely that the 1232-cm^{-1} band arises from the CH_2 twisting vibration[45] and that the remaining bands are due, in part, to the amide III vibration. This conclusion is in qualitative agreement with the previous work of Jakes and Krimm.[3] A fourth band at 953-cm^{-1} shifts 5 cm^{-1} lower upon ^{13}C labeling and is probably the C–CO stretching vibration. We have not observed the amide IV band in any of the spectra even though Miyazawa et al.[46] have predicted it to be Raman active. It is likely that the bands observed at 1149, 1232, and 1338 cm^{-1} are the Raman analogues of the amorphous band and the two regular conformation fold bands observed in the infrared spectra by Starkweather and Moynihan[23] and Koenig and Agboatwalla,[25] respectively. The Raman analogue of the 936-cm^{-1} crystalline infrared band[23-27] does not appear to be present. The temperature dependence of these bands should be useful in confirming their origin.

The sum spectrum (SUM) constructed for this region with the same procedure as used above for the C–H stretching region is very similar from 1200 to 1700 cm^{-1} to the spectrum of the unlabeled NYL66 (Figure 3). While a high degree of localization of the normal modes is expected in the C–H and C–D stretching regions, the bands in the fingerprint region have generally been thought to be highly coupled. The great similarity of the spectra of the undeuterated NYL66 and the SUM spectrum indicates that, at least for nylon 66, the degree of intrachain vibrational coupling is small. This lack of coupling is surprising in comparison to the amount of coupling that is present in alkanes.[2] It seems plausible that the amide moiety decouples the vibrational motion between adjacent methylene segments, preventing coupling between the segments. Since the amide vibrations are highly localized and essentially do not couple with either the C–H or C–D stretching modes, it would be highly unlikely that any coupling could occur through the amide moiety. Additionally, the lack of substantial perturbations of the Raman spectra upon deuteration would suggest that there is little interchain interaction between the methylene groups. Once again, this would appear to be attributable to the decoupling nature of the amide group, which reduces interchain interactions to a large degree via increased physical separation of the chains relative to polyethylene, where actual crystal field splittings of Raman and infrared bands are observed.

The apparent low degree of coupling in the fingerprint region is further supported by recent NMR studies[47] and molecular dynamics calculations.[48] Both show that the methylene segments in crystalline domains undergo very large amplitude librations that are independent of each other and share no phase correlation. It has also been shown that the amide moiety is relatively static, even near the crystalline melting point, and is evidently pinned into place by the hydrogen-bonded network.

While the results and conclusions reported here are preliminary, they offer the hope that a molecular force field for nylon 66 could be developed from force fields of each of the monomers (derived from a full set of isotopomers) with the addition of monomer-to-monomer interaction force constants (derived from a full set of model isotopomers). Previous efforts[49] to build force fields for nylons from those obtained from analogous small molecules, only some of which were isotopically labeled, have illustrated that in the absence of a full set of isotopomers, this procedure is only partially successfull. Moreover, this approach may be applicable to other polymers but will probably be limited to those macromolecules, such as peptides and proteins, that have decoupling groups which disrupt the vibrational coupling along the backbone. Such force fields would be of great use in developing a more complete understanding of vibrational assignments and molecular dynamics simulations.[50]

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A Spectroscopic Study of Syndiotactic Polystyrene

Fully syndiotactic polystyrene has been recently reported in the literature.[1-8] Only quite recently has the synthetic process been developed;[1,2,7] however, only limited structural information is available. The attractive and interesting physical characteristics of this polymer can be summarized as follows: (1) a melting temperature of 270 °C, (2) a fully trans planar zigzag backbone, and (3) the presence of a solid–solid phase transition.[1,3-6] Because of its inherent backbone stiffness and strong intermolecular interactions, the macroscopic properties such as modulus and strength are expected to exceed those of most polymers, even those of some liquid-crystalline polymers.

A variety of crystal forms have been suggested, including a helical conformation upon crystallization from dilute solution and an all-trans conformation with annealing. The helical phase has been proposed to have a TTGG or T_3GT_3G' conformation.[3,9] We are interested in the nature of these crystalline forms and the amorphous state, and the transition between them. Vibrational spectroscopy is our primary characterization technique. Its sensitivity to local conformation and chain packing changes allows us to observe microstructural changes with annealing, orientation, or solvent treatments. In this paper we examine structural differences between samples of different tacticities observed from their infrared spectra. Evidence will be presented for the presence of two different conformational forms and the transition between them caused by thermal treatment or orientation.

Experimental Section. Polystyrene samples with syndiotacticity greater than 98% were obtained from Idemitsu Kosan Co. Ltd., Japan. Isotactic (90%) and atactic polystyrene samples were obtained from Scientific Polymer Products Inc. and Polysciences Inc., respectively. Thin films were obtained by casting from a 1 wt % solution in chloroform and drying up to 14 days under vacuum at room temperature. Melt-quenched films were prepared by heating the films cast on a AgCl window to 270 °C under a nitrogen atmosphere in order to prevent oxidation and then quenching into liquid nitrogen. Oriented samples were obtained by solid-state coextrusion at 100 °C in a polyethylene billet. Infrared spectra were obtained with a Bruker IFS 113v FTIR spectrometer. Generally 250 scans were collected at a resolution of 2 cm^{-1}. For annealing experiments, samples were heated in a cell constructed in our laboratory. Low-temperature spectra were obtained in a liquid nitrogen cooled cell.

Results and Discussion. The infrared spectra of atactic, isotactic, and syndiotactic polystyrene (sPS) are shown in Figure 1. Large differences in both the infrared and Raman data, related to the different chain conformations of these isomers, are observed, especially in the regions of 540, 750, 900, 1070, and 1200–1400 cm^{-1}. We also found that the vibrational spectra can be perturbed significantly by thermal annealing. The spectra obtained for the sPS generally contain bands that are sharp (approximately 6 cm^{-1} in half-width) as compared to the relatively broad features observed for both isotactic or atactic isomers. From the intensity decrease in the helical bands and the corresponding sharpening of the spectroscopic features observed upon annealing, we intend to show that annealed sPS is of high crystallinity and has a planar zigzag backbone conformation. One of the primary objectives is to seek explicit evidence of vibrations that can be assigned to the all-trans planar zigzag backbone.

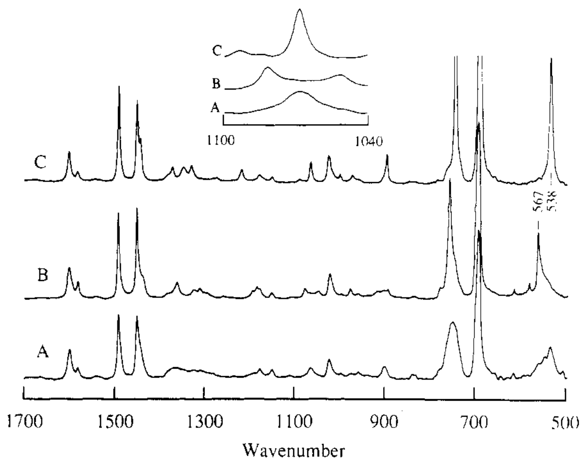

Figure 1. Infrared spectra of (A) atactic, (B) isotactic, and (C) syndiotactic polystyrene.

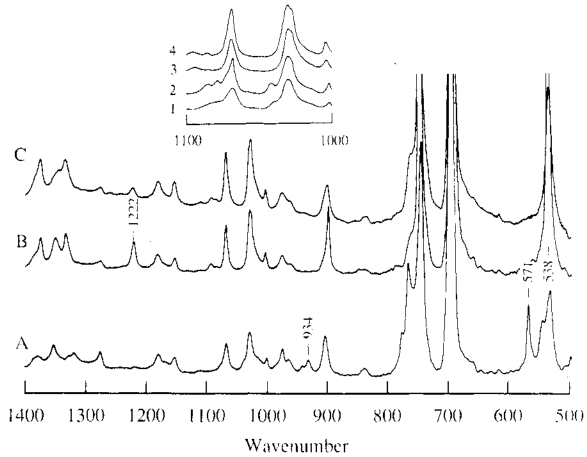

Figure 2. Infrared spectra of sPS (A) as cast, (B) after annealing at 295 °C for 0.5 h, and (C) coextruded at 100 °C to a draw ratio of 4; inset region (1) as cast, (2) at liquid nitrogen temperature, (3) annealed at 200 °C for 1 h, and (4) annealed at 200 °C and measured at liquid nitrogen temperature.

In the 1100–1400-cm^{-1} region, a number of conformation-sensitive skeletal vibrations exist. It is also quite likely that these bands are sensitive to chain packing. The infrared spectrum of the cast film contains spectroscopic features that disappear when the sample temperature is raised. Some of the weak features (1079, 1086, and 1042 cm^{-1}) that are hard to observe at room temperature are seen quite clearly at liquid nitrogen temperature, and this is shown in the inset region in Figure 2. The intensity and position of these weak features are especially sensitive to thermal annealing. One of the more interesting features observed for sPS is the 1030-cm^{-1} band. This band, as-

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