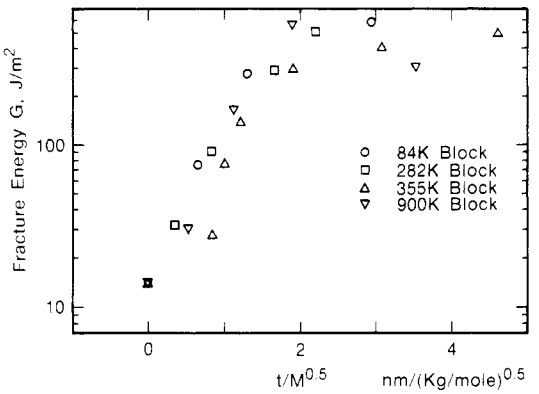

Figure 2. Data in Figure 1 taken with the Instron are plotted to test the relation $G \simeq \exp(t/M^{0.5})$.

from the interface. At this point the block copolymer has a structure similar to that obtained without homopolymer. This observation is consistent with a recent theoretical model for block copolymers at homopolymer interfaces presented by Leibler.[8] From the Instron data for two of the block copolymers (84K and 900K) there is some evidence that the joint toughness decreased a little for $t > t_m$. This observation is consistent with the excess block copolymer forming additional lamellar micelles close to the interface and so forming subsidiary weak interfaces. It is possible that the peak in G at $t = L/2$ (if it exists) is elusive, as it requires a very uniform layer thickness of block copolymer so that the interface is saturated over large areas with little fluctuation in copolymer thickness.

It is evident from Figure 2 that for film thicknesses less than saturation, the toughness G varied exponentially with t and, within the uncertainty of the measurements, could be represented by the form

$$G \sim e^{t/M^{122}} \sim e^{(t/t_m)} \qquad t < t_m \tag{1}$$

This result was unexpected, as a considerable body of crack healing and welding data on polymers has been interpreted by models that relate toughness to the number of strands, σ[16-18] that cross the interface. A number of models exist that differ in detail but none predict that the variation of toughness with σ is greater than a square law. The exponential dependence observed here has not been seen. Also the molecular weight dependence in the relation is surprising. As $\sigma \sim t/M$, it is evident that the number of strands required for a given toughness goes as $M^{-0.5}$. For all the copolymers M is greater than the entanglement molecular weight so one might have expected the toughness to be controlled by σ, independent of M.

The variation of toughness with film thickness might have its origin in the effect of the block copolymer on the thickness of the interface between the PS and PMMA. Fernandez et al.[19] have recently used neutron reflection to measure the thickness of the interface between PS and PMMA homopolymers and obtained a value of less than 20 Å. Anastasiadis and Russell[20] used the same technique to find a value of 54 Å for the interfacial thickness of a PS/PMMA block copolymer, showing that the interface in the block polymer is considerably broader than that between the homopolymers. Noolandi and Hong[6] predicted this effect for the quaternary system containing two homopolymers, a diblock copolymer and a mutual solvent, and suggested its origin in the entropy required to place the block copolymer junction points at the interface. I wish to suggest that such an effect may be occurring here. As block copolymer is added to the interface it broadens, and hence the degree of entanglement between the PS and PMMA chains increases. If, as has been suggested, the interfacial thickness of the pure block copolymer is independent of its molecular weight,[21] then the thickness of the interface between PS segments and PMMA segments might be expected to vary just as its fractional saturation by the block copolymer. Within this argument the exponential form would come from the variation of PS–PMMA entanglement with interfacial thickness and the rapid variation of toughness with entanglement.

The most important observation in this work is that the presence of the block copolymer can increase the toughness of the PS–PMMA interface by up to a factor of 50. The toughness saturates at a block copolymer film thickness equal to half the long period of the neat block copolymer. This suggests that the block copolymer can organize in a simple way at the interface and saturate it. It is perhaps unusual that such morphological information is obtainable from mechanical tests.

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Registry No. PS, 9003-53-6; PMMA, 9011-14-7; (PS)(PMMA) (block copolymer), 106911-77-7.

References and Notes

(1) Fayt, R.; Jerome, R.; Teyssie, Ph. *Polym. Eng. Sci.* **1987**, *27*, 328.
(2) Cohen, R. E.; Ramos, A. R. *Macromolecules* **1979**, *12*, 89.
(3) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Macromolecules* **1970**, *3*, 89.
(4) Gaillard, P.; Ossenbach-Sauter, M.; Riess, G. *Makrol. Chem., Rapid Commun.* **1980**, *1*, 771.
(5) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1989**, *22*, 1449.
(6) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.
(7) Noolandi, J.; Hong, K. M. *Macromolecules* **1984**, *17*, 1531.
(8) Leibler, L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 1.
(9) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.
(10) Russell, T. P. Private communication.
(11) Cho, K.; Gent, A. N. *J. Adhesion* **1988**, *25*, 109.
(12) Wool, R. P.; Willett, J. L.; McGarel, O. J.; Yuan, B. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 38.
(13) Cho, K.; Brown, H. R. Unpublished results.
(14) Brown, H. R. Unpublished results.
(15) Kinloch, A. J.; Young, R. J. *Fracture Behaviour of Polymers*; Applied Science: London, 1983.
(16) Kausch, H. H. *Polymer Fracture*, 2nd ed.; Spinger-Verlag: Berlin, 1987; Chapter 10.
(17) Kim, Y. H.; Wool, R. P. *Macromolecules* **1983**, *16*, 1115.
(18) Adolf, D.; Tirrell, M.; Prager, S. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 413.
(19) Fernandez, M. L.; Higgins, J. S.; Penfold, J.; Ward, R. C.; Shackelton, C.; Walsh, D. J. *Polymer* **1988**, *29*, 1923.
(20) Anastasiadis, S. H.; Russell, T. P. Unpublished results.
(21) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.

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^{15}N NMR Chemical Shift Tensors and Conformation of Some ^{15}N-Labeled Polypeptides in the Solid State

Recently, high-resolution ^{15}N NMR in the solid state has been increasingly applied to the investigation of polypeptides, proteins, and biopolymers.[1-12] In a previous

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Table I
Conformational Characterization of Solid Polypeptides Determined by the ^{13}C CP-MAS NMR, IR, and Far-IR Methods

sample[a]	A/I[b]	^{13}C chemical shifts,[c] ppm					characteristic bands[d]			conformation
			Ala		X					
		amide C=O	C_α	C_β	C_α	C_β	amide I	amide II	far-IR region	
$[Ala^*]_n$	100	176.9	53.2	15.6			1654	1541	527, 374	α-helix
$[Ala^*]_n$-5	5	172.7	48.7	20.8			1630	1548	439	β-sheet
$[Ala^*,Leu]_n$	100	176.3	53.5	15.9	56.2	40.0	1654	1543	473, 398	α-helix
$[Ala^*,Asp(OBzl)]_n$	100	175.0	53.9	16.0	53.9	35.1	1659	1551	494, 453	α-helix
$[Ala^*,Glu(OBzl)]_n$	100	176.1	53.5	16.1	57.4	26.2	1654	1548	409	α-helix
$[Ala^*,Glu(OMe)]_n$	100	176.0 (173.1)		15.7 (20.7)	57.0 (51.7)	26.5	1652 (1628)	1541 (1522)	408	α-helix[e]
$[Ala^*,Val]_n$	100	172.4 (175.0)	49.4	19.2	58.6 (65.3)	33.0 (29.3)	1635	1533	481 (543), 437 (419)	β-sheet[f]
$[Ala^*,Ile]_n$	100	172.5	48.9	20.3	57.8	39.3	1636	1533		β-sheet

[a] Ala* content in $[Ala^*]_n$ and $[Ala^*,X]_n$ is nearly 20% in molar, where X denotes the other L-amino acid residue (natural abundance of ^{15}N). Abbreviations: Ala* = ^{15}N-labeled L-alanyl, Leu = L-leucyl, Asp(OBzl) = β-benzyl L-aspartyl, Glu(OBzl) = γ-benzyl L-glutamyl, Glu(OMe) = γ-methyl L-glutamyl, Val = L-valyl, Ile = L-isoleucyl. [b] Polymerization condition: the molar ratio of the monomer (A) to the initiator (I), which corresponds to the theoretical number-averaged degree of polymerization (n). [c] ±0.2 ppm from $(CH_3)_4Si$; the detectable minor peaks are shown in parentheses. [d] ±2 cm^{-1}: the infrared (IR) and far-IR spectra were obtained for KBr disks with JEOL JIR-FX6160 FT-IR spectrophotometer (4000–200 cm^{-1}); the detectable minor bands are shown in parentheses. [e] Major conformation of $[Ala^*,Glu(OMe)]_n$ is the α-helix form containing small amounts (assumed below 20–30%) of β-sheet form. [f] Major conformation of $[Ala^*,Val]_n$ is the β-sheet form containing small amounts (assumed below 10–20%) of α-helix form.

paper,[13] we have demonstrated that the isotropic ^{15}N chemical shifts of a number of homopolypeptides in the solid state as determined by the cross-polarization magic angle spinning (CP-MAS) method are significantly displaced according to their particular conformations such as the α-helix and β-sheet forms. Moreover, it was found that the ^{15}N chemical shift difference between the α-helix and β-sheet forms of such homopolypeptides in the solid state varies by as much as 1.2–10.0 ppm, depending mainly on the nature of the amino acid residue.[13] Very recently, we have reported that ^{13}C chemical shift tensors are useful for conformational analysis of solid-state polypeptides.[14,15]

According to such experimental findings, the principal values (σ_{11}, σ_{22}, and σ_{33}) of the ^{15}N chemical shift tensors can be expected, in general, to give us much more significant information regarding molecular structure than the isotropically averaged value ($\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$). Especially, it seems very important to elucidate how the anisotropic ^{15}N NMR chemical shift should be affected by the conformation and amino acid sequence of polypeptides or natural proteins in the solid state. In this paper, therefore, we attempt to analyze isotropic ^{15}N chemical shift and individual components of ^{15}N chemical shift tensors of an ^{15}N-labeled L-alanine (Ala*) residue of some polypeptides with α-helix or β-sheet conformation.

^{15}N-labeled poly(L-alanines), $[Ala^*]_n$ and $[Ala^*]_n$-5, and copolypeptides, $[Ala^*,X]_n$, of Ala* with other amino acids (X; natural abundance ^{15}N) were prepared by polymerization of the Ala*-NCA (alanine *N*-carboxy anhydride) and corresponding amino acid NCA in acetonitrile at 30 °C by using n-butylamine as the initiator. All the polypeptide samples contain about 20% of ^{15}N-labeled L-alanine residue. The conformational characterization of these samples was made on the basis of conformation-dependent ^{13}C NMR chemical shifts[16] determined from the ^{13}C CP-MAS NMR method and also by the characteristic bands in the IR and far-IR spectra[17,18] (see Table I).

The solid-state ^{15}N and ^{13}C NMR measurements were performed on a JEOL GX-270 spectrometer operating at 27.4 and 67.80 MHz, respectively, equipped with a CP-MAS accessory. The contact time was 2 (for ^{15}N) and 4 ms (for ^{13}C), and the repetition time was 5 (for ^{15}N) and 4 s (for ^{13}C). A 90° pulse width was typically 5.7 μs for both ^{15}N and ^{1}H under CP conditions and 5.3 μs for both ^{13}C and ^{1}H. Spectral width and data points were 20 (for ^{15}N) and 27 kHz (for ^{13}C) and 8K points, respectively. Spectra were usually accumulated ca. 50 (CP-MAS) and 200 times (static) for ^{15}N and 140–3000 times for ^{13}C CP-MAS to achieve a reasonable signal-to-noise ratio for samples. The ^{15}N chemical shifts were calibrated indirectly by external glycine ^{15}N (δ 11.59; line width = 17 Hz) relative to saturated $^{15}NH_4NO_3$ (δ 0) solution in H_2O. The ^{13}C chemical shifts were calibrated indirectly through external adamantane (29.50 ppm relative to tetramethylsilane $(CH_3)_4Si$). The experimental errors of the isotropic ^{15}N and ^{13}C chemical shift values are estimated within ±0.5 and ±0.2 ppm, respectively. The value of σ_{22} can be read exactly from the observed powder pattern (static) spectra, as shown in Figure 1. For this reason, the error limit of σ_{22} is less than ±0.5 ppm. To obtain the remaining two components (σ_{11} and σ_{33}), we used the values of σ_{iso} obtained by the CP-MAS experiment and of σ_{22} and fitted the theoretical powder pattern line shape[14] which is convoluted with Lorentzian function to the observed powder patterns (Figure 1). Accordingly, the error limit of σ_{11} and σ_{33} is larger (within ±2 ppm) than that of σ_{22}.

The conformations of solid polypeptides determined from the conformation-dependent ^{13}C chemical shifts in the ^{13}C CP-MAS NMR spectra are consistent with those from the characteristic bands in the IR and far-IR spectra. As shown in Table I, it is obvious that the ^{13}C chemical shifts of carbonyl carbon (C=O), α-carbon (C_α), and β-carbon (C_β), as well as the characteristic bands in the IR and far-IR spectra, could be conveniently used for conformational characterization (such as α-helix and β-sheet forms) of solid polypeptides. In particular, the ^{13}C chemical shifts of an individual amino acid residue in a polypeptide are mainly influenced by the local conformation, as defined by the torsional angles (ϕ and ψ) of the skeletal bonds, and not strongly influenced by the specific amino acid sequence.[16]

Table II summarizes the isotropic ^{15}N chemical shifts (σ_{iso}) and anisotropic ^{15}N chemical shift tensors (σ_{11}, σ_{22}, and σ_{33}) of $[Ala^*]_n$ and $[Ala^*,X]_n$, together with anisotropy and asymmetry parameter. The anisotropic ^{15}N chemical shifts (σ_{11}, σ_{22}, and σ_{33}) of the α-helical poly(L-alanine) appear at higher field by −3, 7.3, and 6 ppm, respectively, than those of the β-sheet poly(L-alanine) in the solid state. It is noteworthy for poly(L-alanine) that (1) only σ_{11} of the α-helix form is displaced downfield in comparison with that of the β-sheet form, whereas the other values (σ_{22}, σ_{33}, and σ_{iso}) of the α-helix are displaced upfield in comparison

Table II
Isotropic ^{15}N Chemical Shifts (σ_{iso}), Anisotropic ^{15}N Chemical Shift Tensors (σ_{11}, σ_{22}, and σ_{33}), Anisotropy ($\Delta\sigma$), and Asymmetry Parameter (η) of Polypeptides Containing ^{15}N-Labeled L-Alanine Residues Characteristics of the α-Helix and β-Sheet Forms

sample	conformation	^{15}N chemical shifts,[a] ppm				$\Delta\sigma$[b]	η[c]
		σ_{iso}	σ_{11}	σ_{22}	σ_{33}		
$[Ala^*]_n$	α-helix	98.8	204	54.4	38	158	0.16
$[Ala^*]_n$-5	β-sheet	102.2	201	61.7	44	148	0.18
$[Ala^*,Leu]_n$	α-helix	98.6	204	56.9	35	158	0.21
$[Ala^*,Asp(OBzl)]_n$	α-helix	101.5	208	58.7	38	160	0.19
$[Ala^*,Glu(OBzl)]_n$	α-helix	100.4	206	56.7	39	158	0.17
$[Ala^*,Glu(OMe)]_n$	α-helix	99.9	205	58.1	37	157	0.20
$[Ala^*,Val]_n$	β-sheet	99.7	202	62.4	35	153	0.27
$[Ala^*,Ile]_n$	β-sheet	101.0	200	63.0	40	149	0.23

[a] ^{15}N chemical shifts of Ala* of polypeptides (±0.5 ppm for σ_{iso} and σ_{22} and ±2 ppm for σ_{11} and σ_{33}, from $^{15}NH_4NO_3$). [b] Anisotropy: $\Delta\sigma = \sigma_{11} - (\sigma_{22} + \sigma_{33})/2$. [c] Asymmetry parameter: $\eta = (\sigma_{22} - \sigma_{33})/(\sigma_{11} - \sigma_{iso})$.

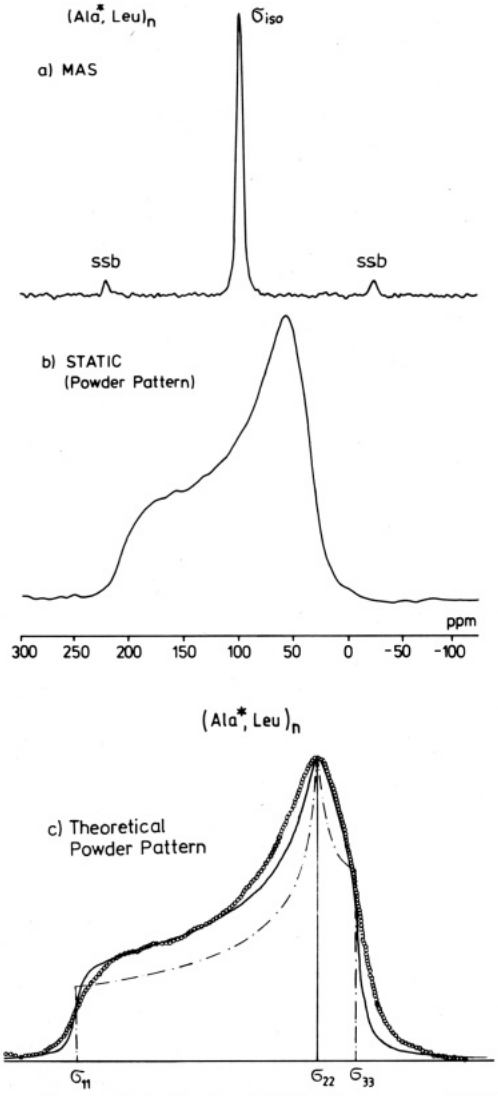

Figure 1. (a) 27.4-MHz ^{15}N CP-MAS NMR Spectra; (b) ^{15}N static (powder pattern) NMR spectra; (c) theoretical powder pattern (-·-) and theoretical powder pattern convoluted with the Lorentzian function (—) and experimental points (O) for $[Ala^*,Leu]_n$.

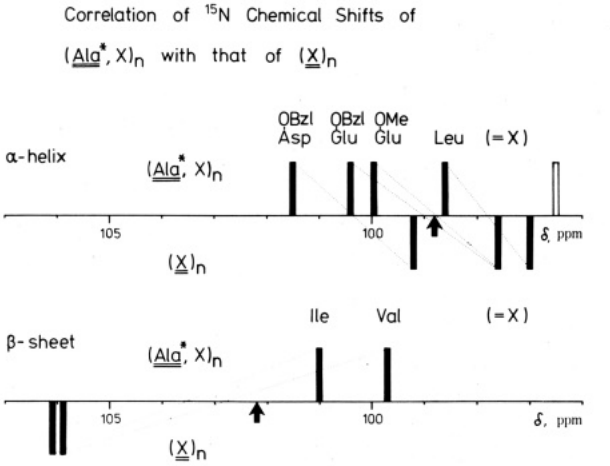

Figure 2. Correlation of the ^{15}N chemical shifts of Ala* of copolypeptides, $[Ala^*,X]_n$, with those of host homopolypeptides $[X]_n$ in the solid state. The arrow indicates the ^{15}N chemical shift of poly(L-alanine).

with those of the β-sheet; (2) the difference of σ_{22} (and σ_{33}) values between the α-helix and β-sheet forms are larger than that of σ_{iso} (3.4 ppm); (3) anisotropy ($\Delta\sigma = \sigma_{11} - (\sigma_{22} + \sigma_{33})/2$) of the α-helix (158) is larger than that of the β-sheet form (148); (4) the asymmetry parameter ($\eta = (\sigma_{22} - \sigma_{33})/(\sigma_{11} - \sigma_{iso})$) of the α-helix (0.16) is not so much different from that of the β-sheet (0.18). According to the recent papers by Oas et al.,[19,20] they have determined the alignment of the ^{15}N chemical shift tensors of L-[1-^{13}C]-alanyl-L-[^{15}N]alanine from the dipole-coupled powder patterns. They assumed that the orientations of σ_{11} (nearly parallel to the N–H bond) and σ_{33} (parallel to the C′–N bond) lie in the peptide plane but that the orientation of σ_{22} is perpendicular to the peptide bond. Accordingly, the ^{15}N chemical shift tensors must be useful for conformational analysis of solid polypeptides, if the origin of the chemical shift displacements can be elucidated. It is necessary to prove the observed ^{15}N chemical shift displacements of poly(L-alanine) between the α-helix and β-sheet forms in the solid state by a theoretical calculation based on an exact molecular orbital theory, which is in progress.

In α-helical copolypeptides $[Ala^*,X]_n$ such as $[Ala^*,Leu]_n$, $[Ala^*,Asp(OBzl)]_n$, $[Ala^*,Glu(OBzl)]_n$, and $[Ala^*,Glu(OMe)]_n$, σ_{iso} of the Ala* appears downfield by 2–3 ppm in comparison with that of the corresponding host homopolypeptide $[X]_n$ (see Figure 2 and ref 13). In β-sheet copolypeptides such as $[Ala^*,Val]_n$ and $[Ala^*,Ile]_n$, in contrast, σ_{iso} of the Ala* appears upfield by 5–6 ppm in comparison with that of the corresponding host homopolypeptide. As a result, the σ_{iso} regions of the Ala* in the copolypeptides with the α-helix (98–102 ppm) and β-sheet forms (98–103 ppm) are overlapping, as Figure 2 shows. This indicates that σ_{iso} of the Ala* depends not only upon conformation but also upon the amino acid sequence of the copolypeptides in the solid state, which is quite a different result compared with that of the ^{13}C chemical shift. However, it is likely that σ_{iso} is useful for determination of conformational change of copolypeptides with

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.

References and Notes

(1) Webb, G. A.; Witanowski, M. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1985**, *94*, 241–290.
(2) Harbison, G.; Herzfeld, J.; Griffin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4752–4754.
(3) Cross, T. A.; Diverdi, J. A.; Opella, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1759–1761.
(4) Cross, T. A.; Frey, M. H.; Opella, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 7471–7473.
(5) Förster, H. G.; Müller, D.; Kricheldorf, H. R. *Int. J. Biol. Macromol.* **1983**, *5*, 101–105.
(6) Huang, T.-H.; Bachovchin, W. W.; Griffin, R. G.; Dobson, C. M. *Biochemistry* **1984**, *23*, 5933–5937.
(7) Stejskal, E. O.; Schaefer, J.; Mckay, R. A. *J. Magn. Reson.* **1984**, *57*, 471–485.
(8) Matthews, C. N.; Ludicky, R.; Schaefer, J.; Stjskal, E. O.; Mckay, R. A. *Origins Life* **1984**, *14*, 243–250.
(9) Cross, T. A.; Opella, S. J. *J. Mol. Biol.* **1985**, *182*, 367–381.
(10) Choi, B. S.; Roberts, J. E.; Evans, J. N. S.; Roberts, M. F. *Biochemistry* **1986**, *25*, 557–561.
(11) Schaefer, J.; Garbow, J. R.; Jacob, G. S.; Forrest, T. M.; Wilson, G. E., Jr. *Biochem. Biophys. Res. Commun.* **1986**, *137*, 736–741.
(12) Stewart, P. L.; Valentine, K. G.; Opella, S. J. *J. Magn. Reson.* **1987**, *71*, 45–61.
(13) Shoji, A.; Ozaki, T.; Fujito, T.; Deguchi, K.; Ando, I. *Macromolecules* **1987**, *20*, 2441–2445.
(14) Ando, S.; Yamanobe, T.; Ando, I.; Shoji, A.; Ozaki, T.; Tabeta, R.; Saito, H. *J. Am. Chem. Soc.* **1985**, *107*, 7648–7652.
(15) Ando, S.; Ando, I.; Shoji, A.; Ozaki, T. *J. Mol. Str.* **1989**, *192*, 153–161.
(16) Shoji, A.; Ozaki, T.; Saito, H.; Tabeta, R.; Ando, I. *Macromolecules* **1984**, *17*, 1472–1479 and references therein.
(17) Miyazawa, T. In *Poly-α-Amino Acids*; Fasman, G. D., Ed.; Marcel Dekker: New York, 1967; Chapter 2 and references therein.
(18) Itoh, K.; Katabuchi, H.; Shimanouchi, T. *Nature, New Biol.* **1972**, *239*, 42–43 and references therein.
(19) Oas, T. G.; Hartzell, C. J.; Dahlquist, F. W.; Drobny, G. P. *J. Am. Chem. Soc.* **1987**, *109*, 5962–5966.
(20) Hartzell, C. J.; Whitfield, M.; Oas, T. G.; Drobny, G. P. *J. Am. Chem. Soc.* **1987**, *109*, 5966–5969.
(21) Harbison, G. S.; Jelinski, L. W.; Stark, R. E.; Torchia, D. A.; Herzfeld, J.; Griffin, R. G. *J. Magn. Reson.* **1984**, *60*, 79–82.

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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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