(2) Ahmed, M. *Polypropylene Fibers—Science and Technology*; Elsevier: Amsterdam, 1982.
(3) Recent reviews can be found in: *High-Speed Fiber Spinning*; Ziabicki, A., Kawai, H., Eds.; Wiley Interscience: New York, 1985.
(4) Vassilatos, G.; Knox, B. E.; Frankfort, H. R. E. *Dynamics, Structure Development, and Fiber Properties in High-Speed Spinning of Polyethylene Terephthalate*; *High-Speed Fiber Spinning*; Ziabicki, A., Kawai, H., Eds.; Wiley Interscience: New York, 1985.
(5) Ziabicki, A. *Fundamentals of Fiber Formation*; Wiley: New York, 1976.
(6) Sadler, D. M.; Barham, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 309–317.
(7) Ballard, D. G. H.; Burgess, A. N.; Nevin, A.; Cheshire, P.; Longman, G. W.; Schelten, J. *Macromolecules* **1980**, *13*, 677–681.
(8) Ullman, R. *J. Polym. Sci. Polym. Phys. Ed.* **1985**, *23*, 1477–1484.
(9) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1984**, *17*, 663–669.
(10) Ballard, D. G. H.; Longman, G. W.; Crowley, T. L.; Cunningham, A.; Schelten, J. *Polymer* **1979**, *20*, 399–405. Ballard, D. G. H.; Cheshire, P.; Longman, G. W.; Schelten, J. *Polymer* **1978**, *19*, 379–385.

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Segmental Dynamics in Nylon 66†

Solid-state NMR methods have been of use in elucidating the dynamics of macromolecules at both the segmental[1] and molecular entanglement length scales.[2,3] At the segmental level this approach has been used to characterize the rates and amplitudes of motion, with great molecular specificity, of both completely amorphous[4,5] and semicrystalline[6,7] polymers. In these systems the experimentally determined mechanics of motion have been used to test various theoretical models of segmental motion.[8] There exist a considerable number of models for methylene chains,[9,10] but in these cases it is experimentally difficult to identify individual chain sites and characterize the different types of motion that each methylene group and its neighbors undergo. We present here a preliminary account of the characterization of segmental dynamics of specifically deuteriated nylon 66 polymers (polyhexamethylene adipamide) that allow us to individually identify the molecular motion that each methylene unit undergoes and thus to examine questions as to the cooperativity of motion. Furthermore, this system has the advantage of allowing us to separately examine subsystems of five and seven bonds which are nominally pinned by the hydrogen-bonding amide sites.

We have prepared specifically isotopically labeled nylon 66 polymers by interfacial condensation polymerization of labeled hexamethylene diamine and adipoyl chloride. The polymers are labeled in one chemically distinct position with either deuterium or carbon-13. The as polymerized polymers have a molecular weight distribution which is skewed to low molecular weight; however, a most probable molecular weight distribution is obtained after equilibrating these polymers in the melt. Polymers that have been selectively deuteriated in the diamine moiety at the C_1 and C_6 carbons (NY16NHME), the C_2 and C_5 carbons (NY25NHME), the C_3 and C_4 carbons (NY34NHME) and in the adipoyl moiety at the C_2 and C_5 carbons (NY25COME) and the C_3 and C_4 carbons (NY34COME) are reported on here.

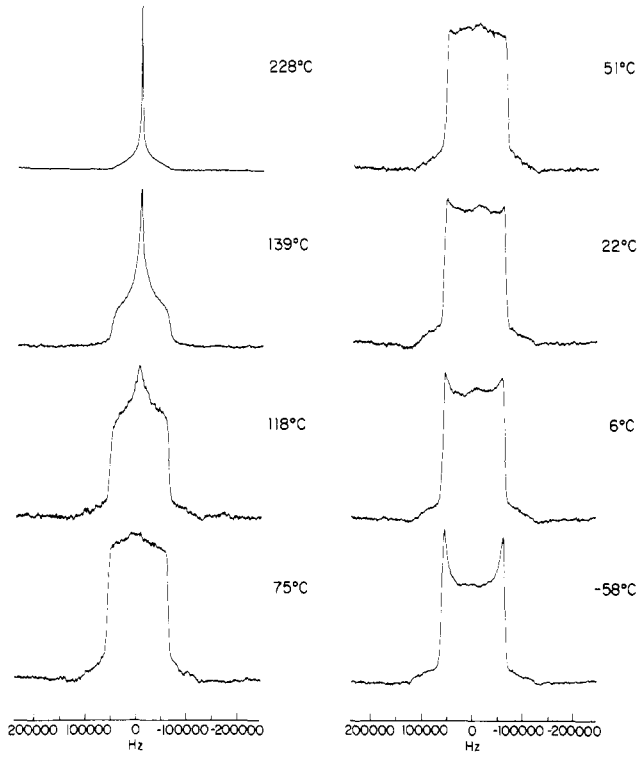

Figure 1. Fully relaxed ^2H NMR spectra at temperatures between −59 °C and 228 °C of nylon 66 that has been selectively deuteriated at the C_1 and C_6 carbons of the diamine moiety.

Figure 1 illustrates temperature-dependent fully relaxed ^2H NMR spectra of nylon 66 polymer labeled with deuterium on the carbons α to the nitrogen. These spectra were obtained with a Bruker MSL-200 NMR spectrometer at a resonance frequency of 30.7 MHz with a quadrupole echo sequence employing a $\pi/2$ radiofrequency pulse length of 2.8 μs and a delay between the quadrature pulses of 20 μs. The spectra are all acquired without symmetrization (no zero filling or data blanking). These spectra contain contributions from both the crystalline and noncrystalline regions of the polymer; however, it is clear that at temperatures above the glass transition temperature (>75 °C at the frequency of this measurement (~100 kHz)) we observe a very narrow component in the line shape which is attributable to methylene groups in noncrystalline domains undergoing essentially isotropic motion that is fast on this time scale. Furthermore, at the lowest temperature illustrated (−58 °C) the spectrum can be approximated as a Pake doublet indicating that we are in the slow-motion limit for all methylene groups α to the nitrogen regardless of the morphology of their environment. These data may be decomposed into components identified with methylene groups in either crystalline or noncrystalline environments by T_1 discrimination experiments; comparison of these results to other measures of crystallinity indicate that the long T_1 component may be quantitatively identified as arising from the crystalline domains and the short T_1 components with the noncrystalline domains. A full line-shape analysis of the decomposed line shapes will be presented in papers to follow.

† Contribution no. 4657.

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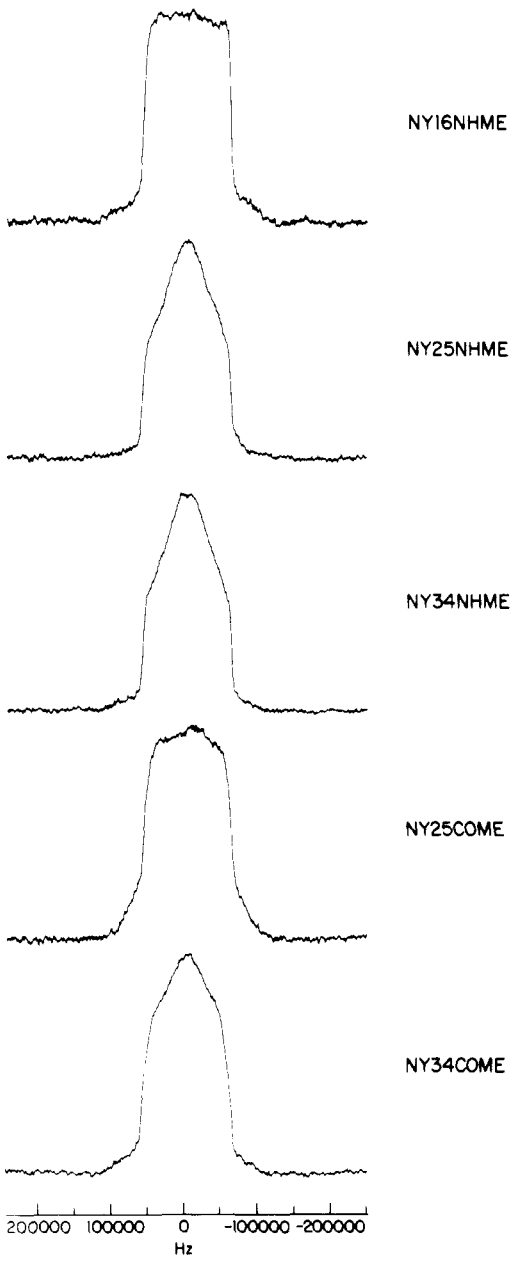

Figure 2. Fully relaxed ^2H NMR spectra at 97 °C of nylon 66 polymers that have been selectively deuteriated in the diamine moiety at the C_1 and C_6 carbons (NY16NHME), the C_2 and C_5 carbons (NY25NHME), and the C_3 and C_4 carbons (NY34NHME) and in the adipoyl moiety at the C_2 and C_5 carbons (NY25COME) and the C_3 and C_4 carbons (NY34COME).

Figure 2 illustrates fully relaxed ^2H NMR spectra at 97 °C for each of the nylon 66 polymers that have been selectively deuteriated on the five chemically distinct methylene carbons. These spectra illustrate that the type of motion extant at each methylene site is not the same. A qualitative interpretation of these line shapes indicates that the motion at both pairs of methylene carbons α to the amide linkage are motionally inhibited relative to the interior methylene groups. A full analysis of the dynamics of each methylene group including the temperature dependence and the heterogeneity of the rates and amplitudes of librational and internal rotation modes is in progress. Preliminary results for each of the methylene groups in the crystalline domains indicate that there is considerable internal rotational freedom as well as librational motion well below the melting point and the motion of all five methylene groups is quite similar at all temperatures above the Brill transition. Methylene groups in the noncrystalline domains exhibit substantial internal rotational motion as well as libration substantially below the glass transition temperature and the motion of both pairs of methylene groups α to the amide linkage is inhibited relative to that of the interior methylenes. These data should allow a critical examination of various models[9,10] of macromolecular dynamics at the segmental level.

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References and Notes

(1) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(2) Cohen-Addad, J. P. *Polymer* **1983**, *24*, 1128.
(3) English, A. D. *Macromolecules* **1985**, *18*, 178.
(4) Jones, A. A. In *Molecular Dynamics in Restricted Geometries*; Klaster, J., Drake, J. M., Eds., Wiley: New York, in press.
(5) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polym. Sci.* **1987**, *265*, 815.
(6) Vega, A. J.; English, A. D. *Macromolecules* **1980**, *13*, 1635.
(7) Hentschel, D.; Sillescu, H.; Spiess, H. W. *Polymer* **1984**, *25*, 1078.
(8) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.
(9) Stockmayer, W. H. *Pure Appl. Chem. Suppl. Macromol. Chem.* **1973**, *8*, 379.
(10) Helfand, E. *Science (Washington, D.C.)* **1984**, *226*, 647.

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Static Light Scattering Studies of Suspensions of Charged Rodlike Tobacco Mosaic Virus

Static light scattering (SLS) in the visible region is a suitable technique to study structural properties of interacting polyelectrolyte systems. The accessible scattering vectors q range from 0.6×10^{-2} nm^{-1} to 3.3×10^{-2} nm^{-1} at a wavelength $\lambda = 488$ nm. A thoroughly studied model system for spherical polyelectrolytes are charged polystyrene spheres (latex) in aqueous solution.[1,2] In order to investigate the influence of structural anisotropy one can choose the model of stiff rods. The tobacco mosaic virus (TMV) particle with length $l = 300$ nm, diameter $d = 18$ nm, and surface charge of about 1000 e$^-$ is a good example of this type.[3] LS work has been reported concerning its dynamic properties in buffer solutions.[4] However, no attention has been paid to effects of interaction at very low ionic strength, which have been shown to become strong in the case of latex spheres. Almost nothing is known either experimentally or theoretically about the interaction potential between highly charged nonspherical finite sized Brownian particles and about the resulting structural correlations in such systems. Allowing for flexibility of the linear particles, a large number of systems have been investigated of which we would like to mention NaPSS since

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