not been found yet owing to the difficulty of obtaining accurate values for the thermodynamic parameters of polymerization for a homologous series of monomers. However, this paper appears to present the first confirmation of a steric effect of the monomer substituents on the polymerization in a quantitative sense. The present conclusion is surely not applicable yet to the polymerizations of a wide range of monomers.

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Solvent Dependence of the Chain Dimensions of Poly[illegible]xyl isocyanate)

Robert Cook*

Lawrence Livermore National Laboratory, Livermore, California 94550

Robert D. Johnson,* Chas. G. Wade, and Daniel J. O'Leary

IBM Research, Almaden Research Center, San Jose, California 95120

Beth Muñoz and Mark M. Green*

Department of Chemistry and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201

Received November 16, 1989; Revised Manuscript Received January 30, 1990

ABSTRACT: Poly(*n*-hexyl isocyanate), known to be a stiff helical polymer, is found experimentally to have persistence lengths of from 20 to 40 nm, depending upon the solvent in which the measurements are made. The origin of this solvent dependence is hypothesized in the present work to be due to a local interaction of polar solvents with the chain backbone, giving rise to greater torsional oscillations around the backbone bonds. NMR line-width measurements made on the same sample of polymer in a variety of solvents support this idea by showing that the magnitude of the polymer's local motion is correlated with solvent polarity.

Introduction

Poly(*n*-alkyl isocyanates)[1–7] have been known for some time to be stiff rod-like macromolecules, particularly when viewed on a short length scale.[2–7] It is generally accepted that the rod-like structure is a result of a helical twist to the chain, which arises from a competition between electronic and steric factors.[6,7] The structure of the crystalline state also reflects this feature, exhibiting a repeat unit involving eight monomers per three turns.[8] These polymers represent important experimental systems with which to test theories of wormlike chains[9–11] and theories for the formation of liquid crystals.[12] Thus their solution properties have been studied extensively by light scattering and hydrodynamic methods.[4–6,9,13,14] As expected, the molecular rods are not perfectly stiff in solution. This has been demonstrated experimentally by measurements sensitive to the overall chain dimensions, which show a gradual transition from rod-like to coil-like behavior with increasing molecular weight.[4,7,11]

An unusual solvent dependence of the global dimensions of poly(*n*-hexyl isocyanate) that suggests a general decrease in polymer dimension with increasing polarity of the solvent was first uncovered by Schneider et al.[2] and later investigated in greater depth by Berger and Tidswell.[6] This dependence is illustrated in Table I, where the Berger and Tidswell data for the intrinsic viscosity, $[\eta]$, of a $M_w = 2.04 \times 10^5$ fraction are displayed for a variety of solvents whose viscosities, η_{solv}, and dipole moments, μ_{solv}, are also given. The general decrease of $[\eta]$ with increasing solvent polarity is a result of smaller

0024-9297/90/2223-3454$02.50/0

Table I
Solvent Dependence of the Chain Dimensions of Poly(*n*-hexyl isocyanate)

solvent	η_{solv}, cP	μ_{solv}, D	$[\eta]$,[a] dL/g	a_{ex}, nm	$\delta_{C=O}$, Hz	δ_{C_α}, Hz
hexane	0.33	0.0	12.9	42[b]	52	200
CCl_4	0.97	0.0	12.05	–	70	300
toluene	0.59	0.36	10.35	40[c]	31	75
THF	0.49	1.63	10.26	40[d]	20	51
$CHCl_3$	0.57	1.01	8.03	30[e]	25	60
CH_2Cl_2	0.43	1.60	–	20[c]	20	65

[a] Intrinsic viscosities for M_w = 204 000. See ref 6. [b] See ref 13. [c] See ref 25. [d] See ref 6. [e] Persistence length for poly(*n*-butyl isocyanate); see ref 19.

global dimensions in the more polar solvents, as is also shown in Table I by the experimentally determined persistence lengths, a_{ex}.

In contrast to typical random coil polymers where poor solvents cause reduced dimensions, Berger and Tidswell point out that the very large solvent effect observed in poly(*n*-hexyl isocyanate) is *not* due to the long-range thermodynamic effects associated with poor solvents. If this were the case, addition of small amounts of nonsolvent should reduce the polymer dimension, and this is not observed.[6] Thus, they point out that the solvent effects must arise from modifications of the short-range stiffness of the polymer by the solvent.[6] We believe that we have a reasonable explanation for these effects.

There are three ways that the solvent could affect the overall chain dimensions, as measured by $[\eta]$ or a_{ex}, through local interaction. First, it is conceivable that the solvent could alter the nature of the backbone helix by changing the values of the backbone rotational angles. However, small changes of only a few degrees would have only very minor effects on the overall chain dimensions.[15] It is possible that the polymer might take on a completely different helical structure in different solvents, but this is unlikely for the following reasons. Tonelli[16] showed quite clearly that the dipole moment studies of Bur and Roberts[4] are only consistent with the (−40, 160) helix structure suggested by Troxell and Scheraga,[17] which was based on energy minimization calculations and is similar to that found in the crystalline state.[8] Similar calculations by Han and Yu,[18] and also Tonelli,[16] which emphasized slightly different aspects of the potential energy surface, resulted in predictions of very different helices, namely, (±95, ±95) for Han and Yu and (±40, ±40) for Tonelli. If we assume that the (−40, 160) helix is correct for CCl_4, the solvent used in the dipole moment studies, then it seems reasonable to consider one of the other structures for more polar solvents. However, both of the other structures just mentioned would give a more extended and thus stiffer system, all other factors being equal. Further evidence that the helical structure is largely the same in polar and nonpolar solvents arises from measurements of the high-wavelength band in the ultraviolet spectrum, which has been correlated with the helical structure.[19] Measurements of this band for poly(*n*-hexyl isocyanate) in hexane and chloroform at 6 °C give values λ_{max} of 253 and 256 nm and extinction coefficients of 4.7×10^3 and 4.4×10^3 L/(mol·cm), respectively, with nearly identical band shapes. The similarity of these values implies similar helical structures, the slightly higher value in chloroform being consistent with a slightly more planar local structure,[19] a fact that will be shown later to be consistent with our hypothesis. Additionally, the chemical shifts in the ^{13}C NMR spectra for the carbonyl carbon vary by less than 1 ppm over the solvents studied. These small differences can be ascribed to the differences in the solvent environment and are not indicative of different helical structures. Thus, based on this collective evidence we conclude that a gross modification of the helix by the solvent is unlikely.

Tonelli[16] also suggested that the observed rod-to-worm-to-coil behavior of the polyisocyanates with increasing molecular weight might be due to helix reversals which would cause discrete breaks in the rod-like structure. Thus, as a second option to explain the observed solvent dependence, we might propose that polar solvents enhance the likelihood of reversals and thus lead to smaller overall chain dimensions. Statistical thermodynamic analysis of optically active polyisocyanates[20] addresses this point by studying the temperature dependence of the optical rotation of poly((*R*)-1-deuterio-1-hexyl isocyanate)[21] in hexane and chloroform. By appropriate analysis of the data it is possible to extract the approximate energy of a helix reversal and thus the average helical length between reversals. It is found that the minimum contour length between reversals is at least 100 nm, with an average value of ca. 150 nm. These reversals, however, do *not* significantly affect the measured persistence lengths in these solvents, which are between 20 and 40 nm. As shown by Mansfield,[22] the experimentally determined persistence length, a_{ex}, of a polymer characterized by a string of jointed semiflexible rods of average contour length b is given by

$$\frac{1}{a_{ex}} = \frac{1}{a_{to}} + \frac{1 - \cos \rho}{b} \tag{1}$$

where a_{to} is the persistence length the chain would have due only to the flexibility brought about by the oscillations about the backbone rotational angles and bond angles, and ρ is the complement to the angle between breaks. One can easily see that the contribution of the breaks to the observed persistence length is very small, especially when it is recognized that the value of ρ appropriate for a helix reversal as described by Tonelli[16] is ca. 35°. Specifically, given the range of observed persistence lengths of from 20 to 40 nm and a minimum contour length between breaks of 100 nm in these solvents, one can calculate from eq 1 that the persistence length due solely to the backbone oscillations would be 20.6 and 43.1 nm, respectively, for ρ = 35°.

Thus the third and *only* remaining explanation for the unusual solvent effects is that the more polar solvent causes larger torsional oscillations in the chain backbone and thus smaller global dimensions. As shown previously,[24] even small changes in the magnitude of the torsional oscillations can have sizeable effects on the overall chain flexibility as measured by the persistence length. Fortunately, there is an experimental method with which to test this hypothesis.

The resonance line widths in a ^{13}C NMR spectrum of a polymer in solution are strongly dependent on molecular motions. The line width, as well as other relevant NMR relaxation rates, arises from magnetic perturbations which are time dependent. For example, consider the ^{13}C NMR line width of the α-methylene carbon of the hexyl side chain in poly(*n*-hexyl isocyanate). The principal relaxation mechanism will be dipolar, originating from magnetic interactions with the bonded protons, and the effectiveness of relaxation will depend on the length of the internuclear carbon–proton bond as well as the motion of this relaxation vector. For a polymer in dilute solution, the line width can be shown to be proportional to a sum of spectral densities, which represent the motional fluctuations of this relaxation vector at particular frequencies, and generally when the motional cor-

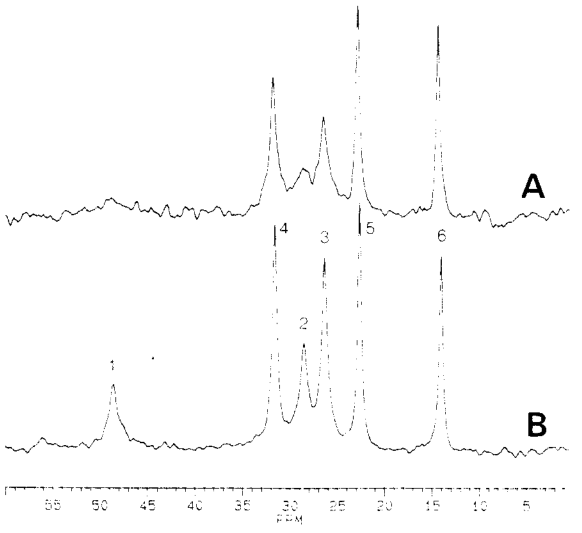


Figure 1. Upfield portions of the 125-MHz ^{13}C NMR spectra of poly(n-hexyl isocyanate) at 308 K dissolved in (A) CCl_4 and (B) $CHCl_3$, showing the hexyl side chain resonances of the polymer. Numbers refer to the position of carbon from the backbone nitrogen. Note that the resonance of the hexyl carbon α to the nitrogen (labeled 1 in trace B) in $CHCl_3$ is significantly narrower than in CCl_4 (trace A), indicating increased mobility at this polymer site in $CHCl_3$. The progressive narrowing of the resonance line widths from carbon 1 to 6 suggests increasing site mobility from the polymer backbone to the methyl terminus of the side chain.

relation times increase, the line width increases (see below). Therefore, if a change of solvent (from hexane to chloroform, for example) results in a significant difference in the observed line width for a particular carbon, it is an indication of changes in the extent of molecular motions for that carbon atom. Similar considerations hold also for the carbonyl carbon. We have therefore obtained the ^{13}C NMR line widths of the α carbon and carbonyl carbon in a sample of poly(n-hexyl isocyanate) in various solvents.

Experimental Section

Poly(n-hexyl isocyanate) was prepared from n-hexyl isocyanate by standard methods as previously reported.[1] M_w values were estimated from measurement of the intrinsic viscosity, using Mark–Houwink parameters determined by Berger and Tidswell.[6]

^{13}C NMR measurements were made on a Bruker AM500 NMR spectrometer, operating at a ^{13}C NMR frequency of 125 MHz at 308 K and were ^{2}H locked. Typically, 100 000 scans per spectrum were collected into 64K points and digitized over a bandwidth of 200 ppm.

Except as noted, the sample had a M_w of 1.31×10^5, and the measurements were made at a concentration of 0.37 g/dL. Line shapes were in all cases Lorentzian, indicating reasonably narrow polydispersity and sufficiently low concentration to avoid complicated interchain interactions.

Results and Discussion

The upfield portions of the ^{13}C NMR spectra of poly(n-hexyl isocyanate) in CCl_4 (A) and $CHCl_3$ (B) are shown in Figure 1. Only the carbons of the hexyl group are shown and are labeled 1–6 relative to the backbone nitrogen. The carbonyl resonance (not shown) is at 157 ppm. The line widths of the carbonyl carbon resonance ($\delta_{C=O}$) and α carbon (δ_{C_α}) of the hexyl group (labeled 1 in Figure 1) in a variety of solvents are listed in Table I. Clearly, the line widths are strongly affected by the nature of the solvent, the lines being in general much narrower in the more polar solvents.

In interpreting the ^{13}C NMR line width in terms of polymer dynamics, we must keep in mind that the possible polymer internal motions are many, and their rates and extent are generally uncharacterized. Following Lipari and Szabo,[23] the scope of the problem is shown by the equation for the dipolar contribution to the ^{13}C NMR line width, δ, which is

$$\delta = 1/\pi T_2 = C(4J(0) + J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H) + 6J(\omega_H + \omega_C)) \quad (2)$$

where the constant C depends on a product of magnetogyric ratios and the inverse sixth power of the internuclear distance, r_{CH}. The spectral densities, $J(\omega)$, are a measure of the motional intensity at the various Larmor frequencies and are given by the real part of the Fourier transform of the time correlation function of the second Legendre polynomial, $P_2(x) = (3x^2 - 1)/2$, of the rotation of the C–H unit vector in the laboratory frame, $\mathbf{u}_{LF}$,

$$J(\omega) = 2\int_0^\infty \cos(\omega t) C(t)\, dt \quad (3)$$

$$C(t) = {}^1/_5 \langle P_2(\mathbf{u}_{LF}(0)\cdot \mathbf{u}_{LF}(t))\rangle \quad (4)$$

Lipari and Szabo point out that in polymers the overall molecular motion (tumbling) will generally be significantly slower than fast internal motions, and the two types of motion will be effectively decoupled. In this limit, $C(t)$ can be written as a product of a correlation function, $C_0(t)$, involving the overall tumbling of the macromolecule, and a correlation function, $C_I(t)$, depending only on the internal motions. Thus

$$C(t) = C_0(t) C_I(t) \quad (5)$$

where

$$C_I(t) = \langle P_2(\mathbf{u}_I(0)\cdot \mathbf{u}_I(t))\rangle \quad (6)$$

The $\mathbf{u}_I$ represent the C–H unit vectors in a frame rigidly attached to the macromolecule. Although $C_0(t)$ is simply given in the isotropic case in terms of a single relaxation time, τ_m, for overall tumbling,

$$C_0(t) = {}^1/_5 \exp(-t/\tau_m) \quad (7)$$

$C_I(t)$ is in general a complex function of the various internal motions. Lipari and Szabo propose that in this limit where the overall tumbling is much slower than internal motions, a model-free analysis is justified, and the relevant parameters of the internal motion can be reduced to two. These are an effective internal correlation time, τ_e, and the square of the order parameter, S^2, equal to the limiting value $C_I(\infty)$ of the internal correlation function. S^2 can vary from 0 to 1, describing the range of internal mobility from a completely flexible system where $C_I(t)$ decays to zero to a rigid system where there is no decay in the correlation ($S^2 = 1$). With these parameters, $C_I(t)$ is then approximated by

$$C_I(t) = S^2 + (1 - S^2) \exp(-t/\tau_e) \quad (8)$$

Using eqs 5, 7, and 8 in eq 3 and assuming rapid internal motions where $\tau_e \ll \tau_m$ and $(\tau_e\omega)^2 \ll 1$, one can show that the spectral densities in the isotropic case have the form

$$J(\omega) = \frac{2}{5}\left(\frac{S^2\tau_m}{1 + (\omega\tau_m)^2} + (1 - S^2)\tau_e\right) \quad (9)$$

When this expression is used in eq 2, the form of the line width reduces to

$$\delta = \delta_0 S^2 + 8C(1 - S^2)\tau_e \quad (10)$$

where δ_0 is the line width for the macromolecule with no internal motion. The polyisocyanate sample, with $M_w = 1.31 \times 10^5$, clearly will have overall rotational correlation times (τ_m in the isotropic case) describing its overall polymer tumbling which is long (e.g., τ_m = tens of nanoseconds) relative to fast internal motions, such as twists or bends, which are characterized by τ_e. Thus, in this case, the line width will be proportional to the product $S^2\tau_m$, the contribution from the terms involving τ_e being negligible. The effects of anisotropy, multiple fast internal motions, and multiple relaxation pathways do not significantly change this result.[23] Thus, for polymers of similar hydrodynamic radius (similar overall rotational correlation times), the observed line width will be reduced from the rigid polymer value by the fraction S^2, which represents the extent of motion of the relaxation vector (e.g. the C–H bond) which is unaffected by fast internal motions. As a simple test for this, we examined a poly(n-hexyl isocyanate) with $M_w = 4.98 \times 10^5$ in $CHCl_3$. Since the hydrodynamic variables scale with molecular weight for these systems,[6] the correlation time τ_m for overall rotational motion should increase by a factor of about 4, with a similar change in the line widths since S is constant. This we observe, as the C_α line width increases from 60 to 250 Hz.

Using the intrinsic viscosities listed in Table I as a guide to the hydrodynamic radii of the polymer in various solvents, we would conclude that if the NMR line widths were dependent only on overall tumbling, they would vary as the intrinsic viscosities do, decreasing by ca. 50% from hexane to $CHCl_3$. Any additional line narrowing must be attributed to increased local motions, that is a decrease in S^2. Before making this comparison, however, we must also take into account the inherent solvent viscosity, η_{solv}, which for polymers with similar hydrodynamic radii will control the tumbling rate and thus the line width. Thus for hexane and CCl_4, which have similar intrinsic viscosities and thus similar hydrodynamic radii, the line widths in hexane are considerably narrower due to the more rapid tumbling in the less viscous solvent. We now can compare the line widths in these solvents with those in $CHCl_3$, where the intrinsic viscosity and thus the hydrodynamic radius is about two-thirds of that in CCl_4 or hexane. By comparing the solvent viscosities and line widths for hexane and CCl_4, we might expect a chain in a *nonpolar* solvent of viscosity equal to that of $CHCl_3$ (0.57 cP) to have line widths intermediate between those in hexane and CCl_4, perhaps ca. 60 and 250 Hz for $\delta_{C=O}$ and δ_{C_α}, respectively. The values of the line widths in $CHCl_3$ are 40% and 24%, respectively, of these values, much less than the values one might expect if only the difference in tumbling rates were important. Thus the additional line narrowing must be due to increased local motions in the more polar $CHCl_3$. It is important to emphasize that comparisons of this sort can only be qualitative and are thus best made between the greatest extremes, as we have done above. The data for toluene certainly indicate some increased local motion, and those for THF considerably more local motion, even when compared with $CHCl_3$. This last observation is somewhat inconsistent with the overall chain dimensions as measured by the intrinsic viscosity or persistence length and will be discussed shortly.

That the line width broadening differences are due to differences in the chain backbone stiffnesses in the various solvents is further confirmed by examining the line widths of the carbons of the hexyl side chain in CCl_4 and $CHCl_3$ as shown in Figure 1. Since the two spectra shown were run at the same concentration, for a given carbon resonance one can compare line widths by noting that they are inversely proportional to the peak heights. Thus, for a specific carbon, a shorter peak is a broader peak. We expect that the effect of the relative backbone stiffness in the two solvents will decrease as we proceed from the C_1 carbon to the terminal methyl carbon, and the line widths of the carbons distant from the chain backbone should be governed only by the relative solvent viscosity differences, which are small. This is in fact observed. Clearly, the resonances for the carbons near the backbone are significantly broadened in CCl_4 (A) relative to $CHCl_3$ (B). However, as we proceed to carbon 6, the peak widths become similar, indicating similar mobility at these sites.

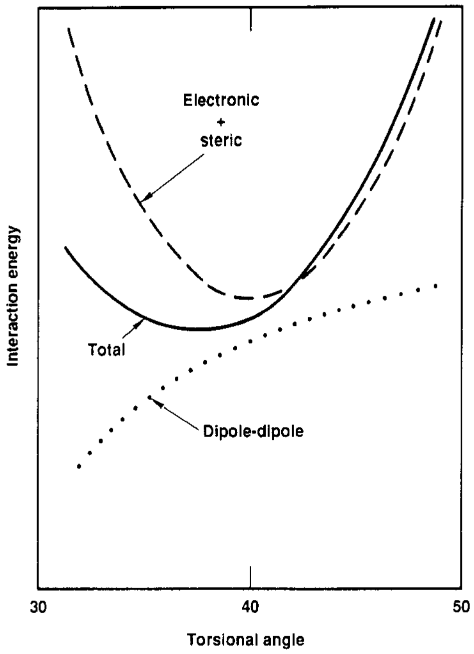
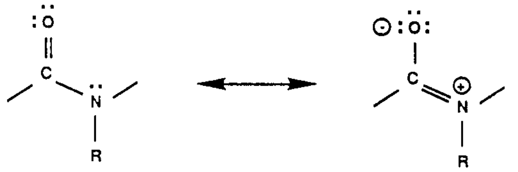


Figure 2. Qualitative representation of the energetic contributions to the backbone torsional angle potential as a function of twist from planarity. Note that the contribution of a dipole–dipole interaction (dots) from the solvent to the intrinsic chain backbone torsional potential (dashes) has the effect of broadening the net or total torsional potential (solid line) that the backbone torsional angles experience.

Although the nature of the solvent–polymer interaction that leads to larger torsional oscillations is open to some speculation, the rough dependence on solvent dipole suggests the following view. In the presence of a nonpolar solvent, the torsional potential has a minimum for each backbone bond which is twisted from planarity by an amount determined by the competition between steric and electronic effects. This potential is qualitatively shown in Figure 2 by the dashed line. As solvent polarity is increased, an additional interaction must be considered, that of the solvent with the chain backbone. The susceptibility to polarization of the local electronic structure will increase as the chain twists toward a more planar state due to the possibility of enhanced delocalization of the π electrons, most simply shown as



Thus as the local chain structure approaches planarity, even slightly, we can expect a greater interaction with a polar solvent leading to enhanced stability for the more planar local structure. This interaction energy as a function of twist away from planarity is shown qualitatively by the dotted line in Figure 2. It is important to note that the strength of this interaction depends not only on the polarity of the solvent but also upon its molecular geometry, which controls how closely it can approach the chain backbone and how well the solvent dipole can orient with respect to the local chain dipole. For this reason comparisons of solvents based on polarity can only be qualitative. It is our assertion, however, that this added stabilization energy in the presence of a polar solvent results in a broadening of the total energy well (solid line, Figure 2) associated with the bond torsion, allowing for larger oscillations and thus a smaller hydrodynamic radius in polar solvents. We also note that this dipolar interaction effect will shift the minimum of the potential slightly toward planarity, an effect which by itself would increase the hydrodynamic radius were it not for the enhanced amplitudes of the torsional oscillations. This shift toward a more planar structure in polar solvents is consistent with the UV measurements discussed above.[19]

The effects described above should be enhanced by strong hydrogen-bonding donor solvents where a hydrogen bond can form between the carbonyl oxygen on the backbone and the solvent. Fetters[26] examined the effects of such a solvent, pentafluorophenol (PFP), and found a steady reversible reduction in the specific viscosity of a solution of poly(*n*-butyl isocyanate) in CCl_4 as a function of the volume percent of PFP, leveling off as the ratio of moles of PFP to moles of butyl isocyanate monomer approached unity. This is consistent with a specific solvent interaction of a single PFP molecule with the carbonyl on the backbone. A reduction by a factor of 5 in the intrinsic viscosity of a nearly monodisperse sample ($M_w = 1.3 \times 10^5$, $M_w/M_n = 1.1$) was also reported for a 20 vol % PFP solution in CCl_4. This decrease is significantly greater than that reported for pure $CHCl_3$ and is consistent with the much stronger specific interaction of the PFP molecules with the chain, as compared to $CHCl_3$.

We note that for THF the large dipole moment and narrow line widths are consistent with our arguments; however, the experimentally determined intrinsic viscosity and persistence length suggest a much stiffer chain. It seems unlikely that there are any significant experimental errors in the Berger and Tidswell[6] data, since both the viscosity and light scattering results are consistent with a relatively stiff chain. Thus, while further experiments may allow a more complete analysis of the specific solvent–polymer interactions in this case, the present data do not allow a more extensive interpretation.

Effects related to the solvent–polymer interaction other than those suggested here may also influence the local rigidity of the backbone geometry. It is clear, however, that the net effect of these interactions is to modify the magnitude of the local torsional oscillations and that the large solvent dependence of the global dimensions of these polymers is due primarily to these modifications rather than to marked changes in helix geometry or to the number of helix reversals.[20,24]

Acknowledgment. R.C. thanks Dr. Lucy Hair of LLNL for several useful discussions. Part of this work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. Work at the Polytechnic University was supported by the National Science Foundation (Grant CHE-8615872) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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