Rod-to-Coil Transition of a Conjugated Polymer in Solution

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A rod-to-coil conformational transition is demonstrated for polydiacetylene, 4-butoxy-carbonylmethylurethane, in solution. With use of quasielastic light scattering, a coillike structure with relatively small hydrodynamic radius is indicated for the polymer in a good solvent, $CHCl_3$. As the proportion of nonsolvent (hexane) is increased, the hydrodynamic radius increases abruptly to a value consistent with the molecule being a rigid rod.

The strong interaction between electronic structure and backbone conformation is a fundamental feature of conjugated polymers. In the case of polyacetylene and other conducting polymers, the chainlike structure leads to strong coupling of the electronic states to nonlinear conformational excitations (solitons and polarons). Much more dramatic changes in backbone conformation and associated electronic structure might be expected for conjugated polymers in solution.

The polydiacetylene system, $+(RC-C \equiv C-CR)_n$, is particularly interesting in this context since with appropriate choice of R group these conjugated polymers will go into solution.[1-5] Moreover, Patel, Chance, and Witt[1] have reported optical- and infrared-absorption studies of an unusual transition involving a major change in electronic structure evidenced by a large shift in the interband transition. They argued that the small interband transition energy found in a "poor" solvent indicates a fully conjugated system (delocalized electronic structure), implying a planar conformation. Similarly, the shift of the transition to higher energy in a "good" solvent was interpreted as evidence that the electrons are limited to short conjugation lengths, implying a nonplanar structure. Resonance Raman studies[5] subsequently confirmed the change in conjugation length.

In this paper, we demonstrate a conformational change for a polydiacetylene, 4-butoxycarbonylmethylurethane (4BCMU), in chloroform/hexane solvent and interpret the results in terms of a rod-to-coil transition. Quasielastic light scattering has been used to determine the diffusion constant, D, and the hydrodynamic radius, R_H, as a function of X_c (the molar fraction of $CHCl_3$ in the solvent). A coillike structure with relatively small R_H is indicated with the polymer in a good solvent, $CHCl_3$. As the proportion of

hexane is increased, R_H increases abruptly to a value consistent with the molecule being a rigid rod. This is the first example of a rod-to-coil transition in a conjugated polymer. The transition observed by light scattering is coincident in X_c with the change in electronic structure.

Light-scattering experiments were carried out on solutions of poly 4BCMU, a diacetylene polymer in which R is $-(CH_2)_4OCONHCOO(C_4H_9)$. The poly 4BCMU used in this study was provided by Dr. R. H. Baughman of Allied Corporation and was prepared in the manner described earlier.[1-4] Patel and Walsh[2] characterized the polymer; they found $n \approx 2400$ corresponding to an end-to-end length of about 1.2 μm.

To prepare the solution samples for light scattering, poly 4BCMU was dissolved in pure $CHCl_3$ and filtered through a 0.5-μm filter. Hexane was then filtered into this solution to the desired solvent ratio. Our experiments utilized a Malvern M2000 correlator and a 15-mW He-Ne laser (6328 Å). The intensity of the scattered light is proportional to $(dn/dc)^2$ where n is the index of refraction and c is the concentration of the scattering species. Thus, for the red solutions ($X_c < 0.55$), where the absorption edge is at ≈ 575 nm,[1] the frequency is in the region of anomalous dispersion; dn/dc is large, making possible the use of very dilute solutions ($< 2 \times 10^{-6}$ g/cm^3). For the yellow solutions ($X_c > 0.6$), the absorption edge is shifted.[1] Thus, at 6328 Å, dn/dc is smaller so that higher concentrations ($\approx 10^{-3}$ g/cm^3) were required to obtain reasonable signal-to-noise ratios for the correlation function.

Patel, Chance, and Witt[1] made a careful study of the phase diagram for poly 4BCMU in hexane/chloroform. They were able unambiguously to distinguish the precipitation (cloud) point from the color transition. As expected, the precipitation point varied considerably with polymer con-

centration whereas the conformational transition occurred at fixed X_c over a range of concentrations spanning more than 2 orders of magnitude. We have extended the spectroscopic measurements to concentrations 2 orders of magnitude smaller. These results demonstrate that the color transition is a purely single-chain phenomenon, and completely rule out bimolecular effects such as aggregate formation. Our light-scattering studies confirm this conclusion. In the red-solution portion of the phase diagram (where the scattering intensity is large), we were able to vary the concentration of poly 4BCMU by more than 3 orders of magnitude with no change in the resulting value for R_H.

Figure 1 shows typical autocorrelation functions obtained for $X_c = 1$ ("good" solvent, yellow solution) and $X_c = 0.4$ ("poor" solvent, red solution) plotted on a semilogarithmic scale. Although deviations from a precise single exponential are evident in both cases (possibly indicative of the polydispersity of the sample), the major effect is the clear change in time scale for the two curves.

In the case of a monodispersed polymer in solution, the time constant for the autocorrelation function appropriate to translational diffusion is given by[6] $\tau = (2Dq^2)^{-1}$ where $q = (4\pi n/\lambda) \times \sin(\theta/2)$. This relation is strictly valid in the

long-wavelength and/or forward-scattering limit where $qR_H < 1$. For larger q, internal modes can also contribute to the decay of the correlation function.[6] Preliminary studies of the angular dependence (θ) verified that in our experiments $\tau \propto q^{-2}$ so that the diffusion constant can be obtained directly from τ. Our measurements were carried out primarily at $2\theta = \pi/2$.

The hydrodynamic radius is obtained from the Stokes equation, $D = k_B T/6\pi\eta R_H$ where η is the solution viscosity, k_B is the Boltzmann constant, and T is the absolute temperature (all experiments reported here were carried out at 300 K). From Fig. 1, we find $2R_H(X_c = 1) = 0.06$ μm and $2R_H(X_c = 0.4) = 0.37$ μm. Note that in the red solutions, the effective diameter of the molecule in solution is nearly 0.4 μm; i.e., close to the end-to-end length of the polymer as a rigid rod. Moreover, since both molecular rotation and internal modes can contribute to the decay, the inferred value for R_H is a lower limit. For an ellipsoid of revolution with semimajor and semiminor axes L and r, respectively,[8] $R_H = L/\ln(L/r)$. Using $2L = 1.2$ μm and $r \sim 20$ Å, one estimates $R_H \sim 0.1$ μm. Thus, the large value found for the red solutions indicates that the conformation is that of a rigid rod. This is qualitatively consistent with the spectroscopic results which imply a relatively long conjugation length.[1] The much smaller value $(2R_H \simeq 0.06$ μm) in the yellow solutions implies a major change in conformation to a coillike polymer.[7] Assuming $R_H = (Ll)^{1/2}$ where l is the persistance length, one finds $l \sim 15$ Å; i.e., again consistent with the spectroscopic results which imply a conjugation length of only a few monomer units.[1]

As X_c was decreased from $X_c = 1$ to $X_c = 0.6$, $2R_H$ remained constant at 0.07 ± 0.01 μm, characteristic of the coillike conformation. For $0.3 < X_c < 0.55$, $2R_H$ was 0.40 ± 0.02 μm, characteristic of the rigid rod. The coil-to-rod transition occurred over the narrow solvent range $0.55 < X_c < 0.6$, as indicated in Fig. 2. The major change in size at the transition can be independently demonstrated by the remarkable observation that the red solution $(X_c < 0.55)$ will not pass through a 0.5-μm filter, whereas the yellow solution $(X_c > 0.6)$ will pass through the same filter.

Titration through the transition starting from $X_c > 0.6$ consistently yielded the yellow-to-red color change and the associated increase in R_H. Titration through the transition from $X_c < 0.55$ is more difficult. Although the color change is evident, a range of values for R_H are obtained.
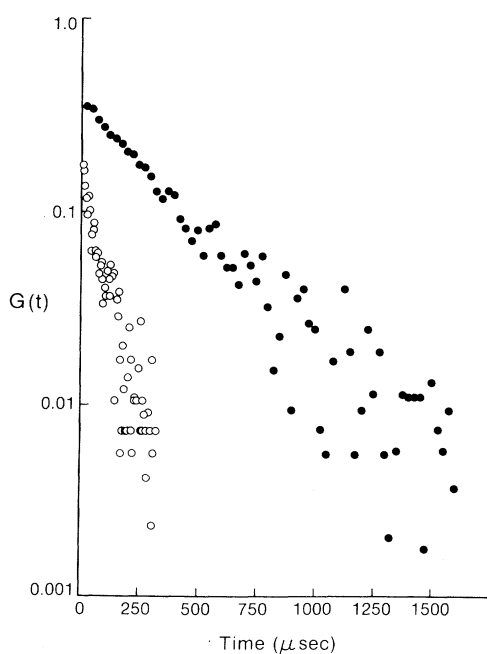

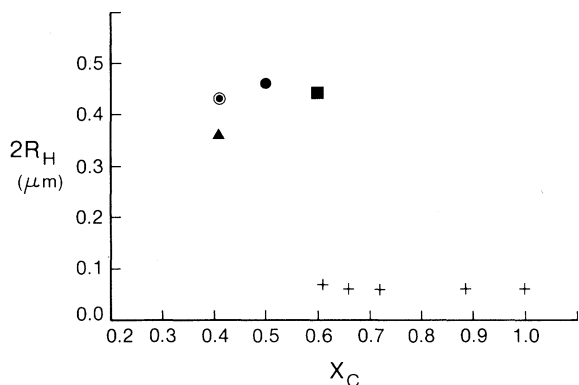FIG. 1. Autocorrelation function, $G(t)$, vs time: open circles, $X_c = 1$; closed circles, $X_c = 0.41$.

FIG. 2. Hydrodynamic radius vs X_c: plus signs, 10^{-3} g/cm^3; circled dot, 5×10^{-6} g/cm^3; triangle, 2.5×10^{-6} g/cm^3; dot, 7.3×10^{-4} g/cm^3; and square, 10^{-3} g/cm^3.

FIG. 3. Schematic diagrams of extreme forms of electronic structure of polydiacetylene: (a) acetylene-like and (b) butatrienelike. The two polymer conformations (rod and coil) are sketched on the right.

However, after careful filtering of the resulting yellow solution, $2R_H \simeq 0.07$ μm is found once again. These observations suggest that entanglement of chains may be important as the rigid rods collapse on going to higher X_c.

The rigid-rod conformation in the poor-solvent regime is perhaps not surprising. The combination of the conjugated backbone and the tendency of successive R groups to form hydrogen bonds[1] (C =O - - - H–N) leads to a rigid planar conformation. In this case, the uninterrupted π system would have a delocalized electronic structure and a long conjugation length. The spectroscopic[1] and Raman data[5] from poly 4BCMU and (more clearly) from poly 3BCMU in the poor-solvent regime are consistent with the planar rigid-rod conformation.

Patel, Chance, and Witt[1] used infrared spectroscopy to study the effect of the conformational transition on the N-H bond stretch. While they found evidence of hydrogen bonding in the planar conformation, the data obtained with the polymer dissolved in CHCl$_3$ indicate that about one out of four N-H groups are not hydrogen bonded. Thus, the mechanism of the transition involves a competition of the CHCl$_3$ solvent with the R-R hydrogen bond resulting in a disruption of the rigid planar structure. The implied ordering of the R groups at the transition is similar to a lyotropic liquid-crystal transition, analogous to the side-chain liquid-crystal transition observed in other polymers.[8]

The origin of the polymer flexibility in the coillike conformation is of interest, for it implies the presence of conformational defects along the polymer backbone. Baughman and
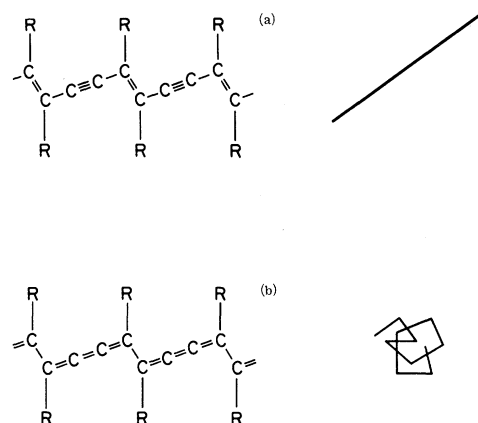
Chance[9] proposed a conjugation-breaking defect (orbital flip defect) corresponding to rotation about the single bond in the acetylenic structure [Fig. 3(a)]. Although such a defect would be effective in breaking the conjugation, the polymer would remain essentially rodlike [rotation about a single bond in Fig. 3(a) by $\pi/2$ leaves the polymer segment in the same direction, with only a minor displacement above or below the plane]. This is not consistent with the $2R_H \simeq 0.06$ μm ($l \simeq 60$ Å) obtained at $X_c = 1$. However, if we assume a butatrienelike structure [Fig. 3(b)], rotation about the single bond will lead to many degrees of freedom and thus to a coillike conformation. In a more detailed description, the flexible joint may be spread over several monomers. Since electron-spin resonance[10] detected no unpaired spins ($<10^{-6}$ spin per polymer chain!), whatever the nature of the conjugation-breaking defect, it does not involve the formation of a singly occupied localized electronic state.

In summary, quasielastic light scattering from polydiacetylene (4BCMU) in solution has provided direct evidence of a conformational transition as the solvent ratio (chloroform/hexane) is varied. In the rod conformation, the electronic wave functions are delocalized, whereas in the coil conformation the wave functions are localized over a few monomer units. The flexibility of the coil arises from a combination of breaking the R-R hydrogen bonding and rotation about the single bond in the butatriene structure of the carbon backbone.

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