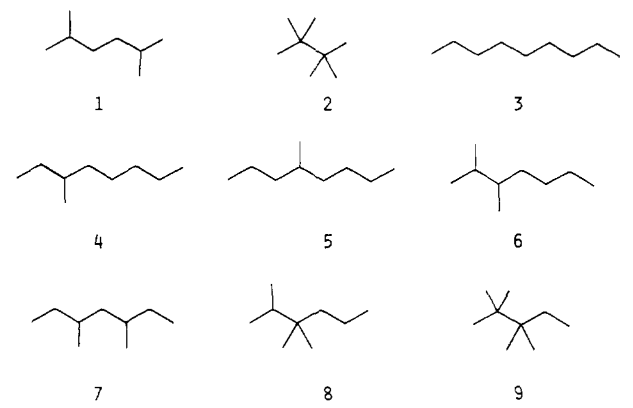

Figure 1. Molecular graphs for alkanes having the same L index 15.

Table I. Molecular Path Counts p_1, p_2, and p_3 and Carbon-13 Chemical Shift Sums for Alkanes with L = 15

no.	p_1	p_2	p_3	chemical shift sum (ppm)
1	7	8	5	220.2
2	7	12	9	223.6
3	8	7	6	225.4
4	8	8	7	226.9
5	8	8	7	228.6
6	8	9	8	225.1
7	8	9	8	228.8
8	8	11	10	227.2
9	8	13	12	229.1

which accounts for a single molecule, Randič[16] reported that sums of carbon-13 chemical shifts for all atoms in 18 octanes correlate with molecular path counts. He found that p_2 makes a positive contribution, while p_3 makes a negative one to the molecular isomeric variations. Recently Randič and Trinajstic[17] have found that the difference ($p_2 - p_3$) leads to a correlation of mean carbon-13 chemical shifts in octanes and nonanes. However, they did not report the regularities of chemical shift sums for molecules of diverse composition and constitution. Randič[18] also found the regularities of carbon-13 chemical shifts for individual atoms in alkanes.

We have extended the work of Randič[16] on the chemical shift sums and found a simple relation between an integer graph theoretical index L and the chemical shift sum. L is defined as

$$L = 2p_1 + p_2 - p_3 - 2 \qquad (1)$$

The experimental chemical shift values for 64 alkanes[13,14] from C_2 through C_{10} relative to tetramethylsilane were used in this study. The relatively large spread of the values for carbon-13 chemical shift sums, from 11.4 for ethane to 312.1 for 2,2,4,4-tetramethylpentane was observed. The molecular path counts p_1, p_2, and p_3 and carbon-13 chemical shift sums for nine alkanes with L = 15 are shown in Table I. The molecular graphs for these alkanes are shown in Figure 1. It is worthy to remark that the skeletal forms shown in Figure 1 are so distinctive, and there is not a priori reason to expect that these molecules will share any common characteristics; however the present work points out that they have common chemical shifts sum.

In Figure 2 we plotted the chemical shift sum $\sum\delta$ against the L index for 64 alkanes. All the points of the plot in this figure can be fitted reasonably well on one straight line. $\sum\delta$ has been shown to be proportional to L:

$$\sum\delta \propto L \qquad (2)$$

Using a least-squares regression analysis, we computed the slope of this straight line. The slope was found to be 14.9 ppm, and the correlation coefficient was 0.992. The predicted chemical shift sum for the alkanes with L = 15 shown in Table I is 223.5 ppm.

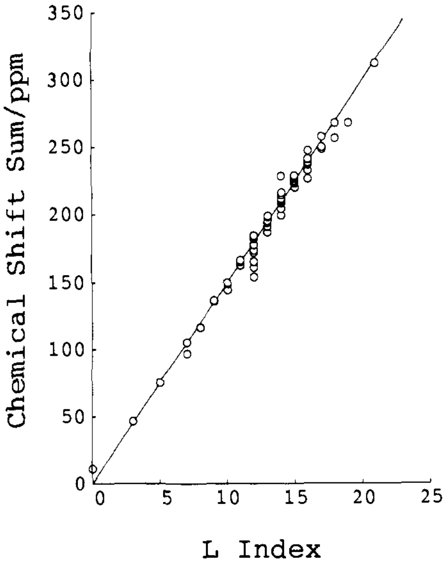

Figure 2. Plot of the carbon-13 chemical shift sum against the L index for alkanes from C_2 to C_{10}.

From eq 1, it is easy to understand the effect of path counts on the chemical shift sum: p_1 and p_2 make a positive contribution, while p_3 makes a negative one to the diverse homological variations in alkanes. The new graph theoretical index L is useful for classifying alkanes into global C-13 nuclear magnetic categories. The simple sum of chemical shift in the alkane has been shown to be one of the characteristic molecular properties which reflect simple but relevant features.

In summary, a novel relationship between molecular path counts and chemical shift sums has been discovered. Details of this work concerning the relation between the additivity of individual chemical shifts for atoms and chemical shift sums in alkanes and statistical analysis are being published elsewhere.

Acknowledgment. We thank the Computer Center, Institute for Molecular Science for affording us facilities for computation.

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Photomodulation of Polypeptide Conformation by Sunlight in Spiropyran-Containing Poly(L-glutamic acid)

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Photochromic vinyl polymers, such as polyacrylates containing spiropyran groups, were found to undergo photoinduced variations of their viscosity.[1-4] Since the viscosity of a polymer system is

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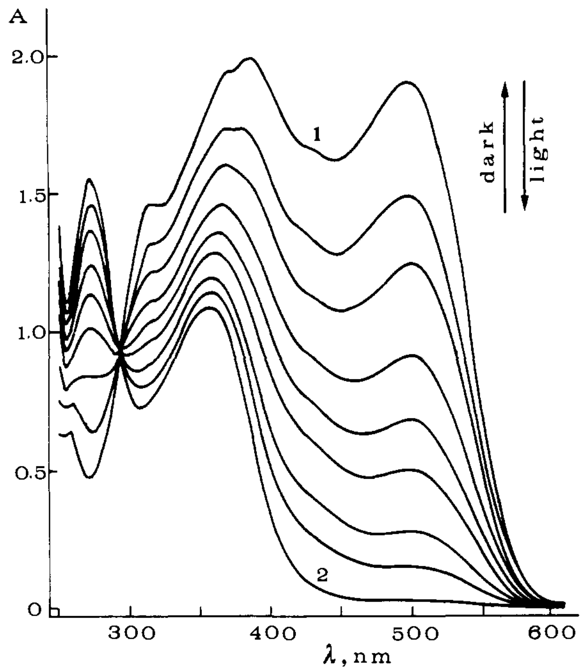


Figure 1. Poly(L-glutamic acid) containing 41 mol % spiropyran units, in HFP ($c = 6.28 \times 10^{-2}$ g/L). Variation of the absorption spectra as a function of irradiation and dark adaptation time: 1, dark adapted solution; 2, photostationary state upon exposure to sunlight or irradiation at any wavelength in the range 350–570 nm.

in part a reflection of polymer conformation, the "photoviscosity effects" were generically attributed to photoinduced conformational changes of the macromolecules.

From the point of view of conformational properties, photochromic polypeptides are much more attractive systems, since they can exist in definite ordered structures such as α-helix or β-structures, and their conformational variations can be directly investigated by means of CD measurements.[5-9] In addition, their structure is much more relevant to the proteic nature of biological photoreceptors.[10,11]

In this context we report the first preparation of a photoresponsive polypeptide containing spiropyran units in the side chains[12] and clear CD evidence that the polypeptide can undergo large random coil ⇌ α-helix conformational changes upon exposure to sunlight and dark conditions, alternately. Moreover, irradiation in solvent mixtures having appropriate compositions allows the extent of the photoresponse to be controlled.

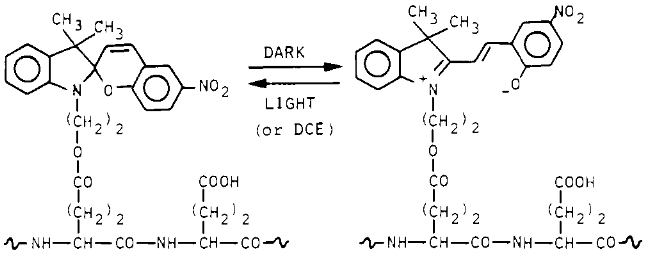
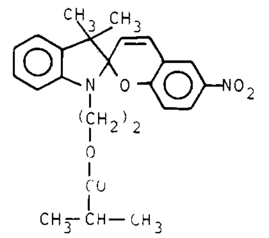


Figure 2. Photochromic behavior of spiropyran-modified poly(L-glutamic acid) in HFP.

Poly(L-glutamic acid) ($\bar{M}_v$ = 250 000) (1.6 mmol Glu residues) was reacted with 1-(β-hydroxyethyl)-3,3-dimethyl-6′-nitrospiro(indoline-2,2′[2*H*-1]benzopyran)[13] (3.2 mmol), in the presence of dicyclohexylcarbodiimide (1.6 mmol) and 4-pyrrolidinopyridine[14,15] (1 mmol), in anhydrous dimethyl formamide for 24 h at room temperature. The polymer was precipitated in ethanol and redissolved in DMF. Precipitations and dissolutions were repeated to the complete removal of any unreacted reagent. The dried polymer resulted soluble in hexafluoro-2-propanol (HFP) only. A content of about 41 mol % spiropyran units was evaluated by comparing the absorption spectrum with that of the low molecular weight spiropyran compound I, corresponding to the 2-methylpropanoyl ester of the same spiropyran (spiro form: λ_{max} = 355 nm; ϵ_{max} = 11 200 M^{-1} cm^{-1} in HFP).



I

In HFP, both the modified poly(L-glutamic acid) and the compound I exhibit intense "negative" photochromism:[16] at room temperature in the dark, in fact, they give orange-colored solutions which are bleached by irradiation with visible light or by mere exposure to sunlight for a few seconds.[17]

The dark-adapted HFP solution of the polymer is characterized by a broad absorption in the range 550–280 nm, with relative maxima at 495, 385–365, and 312 nm (Figure 1). The model compound I shows a similar set of absorption bands, even though the maxima have different relative intensities.[18] On irradiation, the absorption in the visible range of the spectrum is completely cancelled. At the photostationary state the spectra of the polymer and the model are very similar with absorption maxima at 355 and 272 nm.

In the dark at 25 °C, the original spectrum is reversibly restored in about 24 h (half-life time = 2.5 h for the polymer and 1.2 h for the model, respectively). The recovery of the thermodynamically stable species in the fluorinated solvent HFP is much slower than the decay of the spiropyran compounds occurring in common organic solvents.[16] In chloroform, the thermal decay of the model compound I from the colored form to the colorless one occurs at a very high rate (half-life time = 18 s).

These reversible processes can be assigned to the well-known isomerization reaction between the colorless closed spiro structure and the colored ring-opened merocyanine structure (Figure 2).

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(18) The relative different intensities of the maxima between the polymer and the low molecular weight compound are likely to be due to a different equilibrium between various colored species, including various stereoisomers, dimers, and higher aggregates. In the polymer, protonation of the open form by unmodified -COOH functions may also occur: (a) see ref 15 and 16. (b) Smets, G. *Adv. Polymer Sci.* **1983**, *50*, 17–44. (c) Kalisky, Y.; Williams, D. J. *Macromolecules* **1984**, *17*, 292–296.

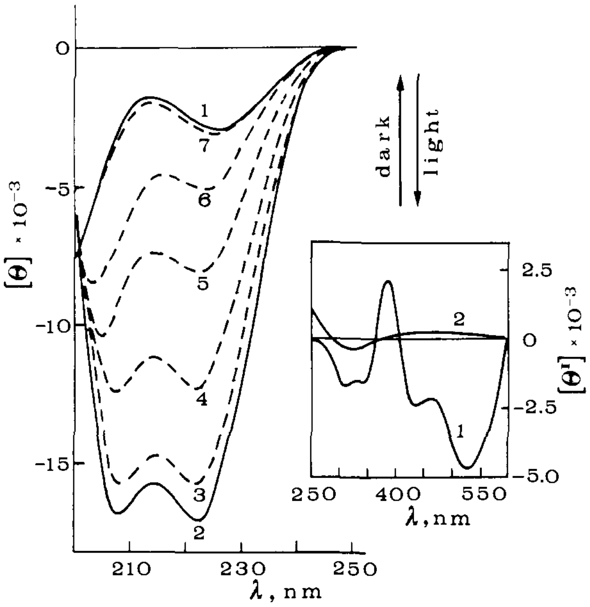

Figure 3. Spiropyran-containing poly(L-glutamic acid) (41 mol %) in HFP ($c = 6.28 \times 10^{-2}$ g/L). Effect of irradiation and dark adaptation on CD spectra: 1, dark adapted solution (colored form); 2, after exposure to sunlight or photostationary state at any wavelength in the range 350–570 nm (bleached form); 3–7, thermal recovery of the colored form at 25 °C, after 36 min (3); 98 min (4); 198 min (5); 324 min (6); 24 h (7). Below 250 nm, CD data are expressed in terms of molar ellipticity $[\Theta]$, based on the mean residue molecular weight. Above 250 nm, the molar ellipticity $[\Theta']$ is referred to one spiropyran-glutamyl residue.

The negative photochromic behavior is likely to be due to the high polar solvent HFP which stabilizes the zwitterionic merocyanine more than the apolar spiro form. This is confirmed by the ^{13}C NMR spectra. In the colorless solution the resonances of 3,3-dimethyl groups appear as two separate peaks, at 27.0 and 21.0 ppm, as a consequence of the presence of the chiral C(2) spiro carbon atom. In the colored solution, by contrast, the two methyls appear as one singlet at 28.7 ppm, suggesting that the spiro carbon atom has lost its dissymmetry assuming a planar structure.

The CD spectra show that the polypeptide chain adopts an essentially random coil conformation in the dark, where the photochromic side chains are in the merocyanine form. Weak CD bands are also present in the visible range of the spectrum (Figure 3). The bleached solution after exposure to visible light displays the typical CD pattern of the α-helix, indicating that the isomerization of the side chains from the cyanine to the spiro form causes the spiralization of the polypeptide chain. The back-reaction to the colored form in the dark is accompanied by the progressive decrease of the helix content and recovery of the original disordered conformation (Figure 3). The reactions are fully reversible.

The key factor responsible for the photoresponse effects is likely to be the interactions among the photochromic side chains, which are different when they are in the charged merocyanine form or in the apolar spiro form. Actually addition of increasing amounts of 1,2-dichloroethane (DCE) to the HFP solution shifts the equilibrium toward the spiro form (Figure 2). Of course, the spiro species content in the dark-adapted solution changes with the HFP/DCE composition, so irradiation at selected solvent compositions makes it possible to control the intensity of the photoresponse. At HFP/DCE v/v ratios 100/0, 70/30, and 50/50, the photoinduced helix contents are respectively 45%, 35%, and 30%.[19]

Acknowledgment. D. F. thanks ENI-ROMA for a Ph.D. fellowship.

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Neutron Diffraction Structure Analysis of a Hexanuclear Copper Hydrido Complex, $H_6Cu_6[P(p\text{-tolyl})_3]_6$: An Unexpected Finding

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The exact structures of hexameric copper(I) hydrido species have been the subject of considerable debate, particularily with regard to the location of the spectroscopically elusive hydride ligands.[1-5] In the original work on $H_6Cu_6(PPh_3)_6$, neither the NMR nor the IR exhibited features identified with the H ligands.[1] Indeed, it has been speculated that, in solution, this complex (and related species) probably exists as a mixture of various oligomeric forms.[5] At any rate, the solid-state structure of $H_6Cu_6(PPh_3)_6$ showed a central Cu_6 octahedron with six long (average 2.655 (17) Å) and six short (average 2.542 (44) Å) Cu–Cu distances, and it was concluded that the unlocated H ligands were probably situated on the six long Cu–Cu edges.[1] Some years later, we examined the structure of the closely related $H_6Cu_6[P(p\text{-tolyl})_3]_6$ cluster and reached the same conclusion.[2] In the meantime, it was suggested by Stucky and co-workers[3] that the H ligands might be located on the faces rather than the edges of the octahedron; and this was found to be the case in a different hexameric cluster, $H_6Cu_6[P(NMe_2)_3]_6$, by Caulton, Huffman, and co-workers using low-temperature X-ray techniques.[4] In the present communication we report a single-crystal neutron diffraction analysis of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ which shows that, contrary to our earlier expectations,[2] the six H atoms in that cluster are situated at face-bridging positions rather than edge-bridging ones.

In our early attempts to grow large crystals of $H_6Cu_6(PPh_3)_6$ for a neutron diffraction analysis, we quickly became aware of a major obstacle: Namely, the triphenylphosphine derivative[1] tended to crystallize out in thin flat plates, unsuitable for neutron diffraction studies. However, the structurally similar $P(p\text{-tolyl})_3$ complex[2] crystallized in a prismatic habit, more suitable for the growth of large specimens, and by a variation of solvents and crystallization techniques we were able to achieve the crystal size and quality required for a neutron diffraction analysis. The crystal used in the present study was grown from a benzene/toluene/tetrahydrofuran solution (approximately 2:1:1) with pentane as precipitant and utilizing standard drybox techniques.

Neutron diffraction data were collected on an automated four-circle diffractometer[6] at the Brookhaven High Flux Beam Reactor, at room temperature, with a crystal of approximate dimensions 3.0 × 4.0 × 2.0 mm.[7] Four main factors arising

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