g of resin (theory, 0.47 mmol/g for 0.5 mmol of NH_2 per g of resin).

These results demonstrate that by reverse-phase suspension polymerization, entirely beaded poly(dimethylacrylamide) resins of predetermined composition can be prepared on a large or small scale.

Experimental Section

Poly(dimethylacrylamide-*co*-*N*,*N*′-bisacrylyl-1,2-diaminoethane-*co*-*N*-acrylyl-1,6-diaminohexane·HCl) (1). (a). Into a three-necked 500-mL, round-bottomed flask, maintained under a nitrogen atmosphere and equipped with a mechanical stirrer, were added *n*-heptane (148 mL) and CCl_4 (83 mL). Freshly distilled dimethylacrylamide (Kohjin, Tokyo) (5.47 g, 55.2 mmol), *N*,*N*′-bisacrylyl-1,2-diaminoethane[12] prepared according to ref 7 (1.1 g, 6.5 mmol), and *N*-acrylyl-1,6-diaminohexane·HCl[11] (0.765 g, 3.7 mmol) were dissolved in water (50 mL). After dissolution was complete, $(NH_4)_2S_2O_8$ (0.15 g) was added and this aqueous solution was added to the organic phase. While the mixture was stirred at 300 rpm, sorbitan sesquioleate (0.3 mL) was added followed by *N*,*N*,*N*′*N*′-tetramethyl-1,2-diaminoethane (0.3 mL). After 40 min the reaction was filtered and the beaded product washed three times with 200 mL each of 2-propanol, $CHCl_3$ (the fines were then removed by flotation in $CHCl_3$), ethanol, water, and ethanol and five times with ethyl acetate. The resin was dried in vacuo for 3 days at 45 °C: yield 6.79 g, 92.5% (7.31 g, 99.6% with fines). Chloride analysis of the hygroscopic resin performed by a modified Volhard method[13] as outlined by Stewart and Young[14] showed 0.47 mmol of Cl^- per g of resin.

(b). A large-scale preparation of 1 using 37.3 g of dimethylacrylamide, 7.5 g of *N*,*N*′-bisacrylyl-1,2-diaminoethane, 5.2 g of *N*-acrylyl-1,6-diaminohexane hydrochloride, and 1 g of $(NH_4)_2S_2O_8$ was performed as in (a). The organic phase consisted of heptane (1043 mL), CCl_4 (565 mL), and sorbitan sesquioleate (2 mL). The reaction was stirred at 600 rpm in a three-necked, 2-L vessel and was initiated by the addition of 2 mL of *N*,*N*,-*N*′,*N*′-tetramethyl-1,2-diaminoethane. The product was washed with 1-L aliquots as described above: yield 49.1 g, 98.2% (49.5 g, 98.9% with fines).

Poly(dimethylacrylamide-*co*-*N*,*N*′-bisacrylyl-1,2-diaminoethane-*co*-*N*-acrylyl-*N*′-Boc-norvalyl-1,6-diaminohexane) (2). A sample of 1 (2 g, 1 mmol of the amino group) was washed for 2 min with 25-mL aliquots of EtOH (thrice), water (thrice), water plus 1 N NaOH (1.0 mL) (10 min), water (five times), EtOH (four times), and CH_2Cl_2 (four times). Boc-norvaline symmetrical anhydride[15] (3 equiv), prepared from Boc-Nva (1.3 g, 6 mmol) and dicyclohexylcarbodiimide (DCC) (0.62 g, 3 mmol) in CH_2Cl_2 (25 mL), was added to the resin followed by Et_3N (0.1 mL, 0.7 mmol). After 30 min DCC (0.41 g) was added and after 5 min the beads gave a negative Kaiser test.[16] The resin was washed with 25-mL aliquots of EtOH (thrice) and ethyl acetate (5 times) and then dried in vacuo at 45 °C for 3 days: yield 2 g. Following hydrolysis in 6 M HCl for 22 h at 110 °C, amino acid analysis[17] showed 0.47 mmol of norvaline per g of resin.

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Registry No. 1 71106-43-9; Boc-norvaline, 53308-95-5.

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(12) Specht, E. H.; Newman, A.; Neher, H. T. U.S. Patent 2773063.

(13) Hawk, P. B.; Oser, B. L.; Summerson, W. H. "Practical Physiological Chemistry", 13th ed.; Blakiston: 1954, p 955.

(14) Stewart, J. M.; Young, J. D. "Solid-Phase Peptide Synthesis"; W. H. Freeman and Co.; San Francisco: 1969, p 55.

(15) Hagenmaier, H.; Frank, H. *Hoppe-Seyler's Z. Physiol. Chem.* **1972**, *353*, 1976. Lemaire, S.; Yamashiro, D.; Behrens, C.; Li, C. H. *J. Am. Chem. Soc.* **1977**, *99*, 1577.

(16) Kaiser, E.; Colescott, R. L.; Bossinger, C. D.; Cook, P. I. *Anal. Biochem.* **1970**, *34*, 595.

(17) Moore, S. "Chemistry and Biology of Peptides"; Meienhofer, J., Ed., Ann Arbor Science Publishers: Ann Arbor, MI, 1972; pp 629–53.

ASIS Effect for Tetrahydroselenophene

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Aromatic solvent induced shifts (ASIS) have been determined for tetrahydroselenophene (THS); they are very different from those previously reported by Strom et al. in a study of the ASIS effect on five-membered rings of the type $(CH_2)_4X$, X = CH_2, O, S, Se, CO, and SO_2.[1] These authors used eq 1 to analyze the data with $\gamma_{CCl_4}{}^H$

$$\Delta^H = \gamma_{CCl_4}{}^H - \gamma_{C_6D_6}{}^H \qquad (1)$$

the center of resonance with respect to Me_4Si for a particular kind of proton at infinite dilution in CCl_4 and $\gamma_{C_6D_6}$ the corresponding center of resonance in C_6D_6. The γ values in eq 1 will approach the corresponding chemical shift values (δ) as the system approaches first-order behavior. Except for THS, they found a linear relationship between the solvent shifts (Δ^β) of the β protons and the dipole moments ($\mu_{C_6H_6}$) in benzene. A similar relationship between the solvent shifts (Δ^α) of the α protons and the $\mu_{C_6H_6}$ was not apparent in their work. Since a correlation of the Δ's with dipole moments can be expected in the absence of steric effects in the benzene–solute complex, Strom et al. suggest that steric hindrance perhaps is the cause of the anomaly for the β-proton shift of THS, as well as of the nonlinearity of the α-proton shifts. The same interpretation was given to explain that, contrary to expectation, their value of the dipole moment of THS in CCl_4 is smaller than that in C_6H_6.

The proton chemical shifts and the solvent shifts of the $(CH_2)_4X$ molecules are listed in Table I. The γ_{CS_2} values were obtained by us from the complete analysis of the proton spectra from solutions in CS_2 (molar fraction $\simeq$ 0.1).[2] For tetrahydrofuran (THF) and tetrahydrothiophene (THT) they are only 2.0–2.9 Hz smaller than the γ_{CCl_4} values of Strom et al., while for THS the differences, $\gamma_{CCl_4}{}^\alpha - \gamma_{CS_2}{}^\alpha = 60.8$ Hz and $\gamma_{CCl_4}{}^\beta - \gamma_{CS_2}{}^\beta = 7.0$ Hz, are so large they cannot be explained as either solvent or concentration effects and give rise to the suggestion that different substances were used as solutes. This was later confirmed when we measured the γ_{CCL_4} values of THS that resulted close to those for γ_{CS_2}.

With our Δ values, instead of those of Strom et al., the Δ^β values could be fitted to the straight line

$$\Delta^\beta = 20.0\mu_{C_6H_6} + 5.6 \qquad (2)$$

the average deviation being 1.4 Hz and the largest deviation being 2.2 for cyclopentanone. The Δ^α values could be fitted, except for THF, to the straight line

$$\Delta^\alpha = 12.5\mu_{C_6H_6} + 1.5 \qquad (3)$$

the average deviation being in this case 3.0 Hz. If a second-order function in $\mu_{C_6H_6}$ is used, one obtains eq 4,

$$\Delta^\alpha = 1.2\mu_{C_6H_6}{}^2 + 6.8\mu_{C_6H_6} + 5.5 \qquad (4)$$

the average deviation being reduced to 0.9 Hz. The Δ^α values for THF calculated with (3) and (4) are respectively 18.2 and 16.0 Hz greater than the experimental values.

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Table I. Proton Chemical Shifts of the $(CH_2)_4X$ Molecules[a]

	X							
	CH_2	O	S	Se	Se[b]	CO	SO_2	ref
$\gamma_{CS_2}{}^{\alpha}$		359.4	273.0		279.7			2
$\gamma_{CCl_4}{}^{\alpha}$	150.9	362.1	275.5	340.5	282.1	205.4	291.0	1
$\gamma_{CS_2}{}^{\beta}$		176.7	189.8		197.0			2
$\gamma_{CCl_4}{}^{\beta}$	150.9	179.6	191.8	204.0	198.8	192.2	218.7	1
Δ^{α}	5.3	4.4	21.3	66.4	23.7	35.0	63.8	1
Δ^{β}	5.3	37.5	45.3	63.8	43.6	62.0	99.7	1
$\mu_{C_6H_6}$	0.00	1.69	1.89	1.81	1.81	2.93	4.69	3

[a] All γ and Δ values are in hertz from Me_4Si at 100 MHz, and the dipole moments ($\mu_{C_6H_6}$) are in debye units. [b] This work.

The interpretation of the benzene shifts of the $(CH_2)_4X$ molecules is complicated because the rings are puckered, and their geometry is not fixed. Furthermore, the potential energy barrier to the rotation of the puckering around the ring (pseudorotation) depends on the nature of the functional group, X. Spectroscopic determinations of these barriers provided the values ~0, 50, 773, 1882, and 1687 cm^{-1} for X = CH_2, O, S, Se, and CO, respectively.[4] Correspondingly, the experimental electron diffraction data were found to be in good agreement with the theoretical results by assuming free pseudorotation for cyclopentane and THF and a fast inversion rate between the two half-chair conformations with C_2 symmetry for the other molecules.[5] The interpretation of the proton–proton coupling constants obtained in liquid phase for all these molecules can be satisfactorily carried out, assuming the same conformational behavior found in vapor-phase studies.[2,6] Therefore, the existence of free pseudorotation is perhaps the reason for the anomaly found for Δ^{α} of THF. This effect would be less important for cyclopentane whose small Δ^{α} value is due to its null dipole moment.

Our THS Δ values cannot be considered anomalous as do those of Strom et al., thus suggesting that we really used THS. Furthermore, the mass spectrum clearly indicated that the compound used was THS. Moreover, we have carried out the complete analysis of the proton spectrum of THS and properly interpreted the coupling constants obtained.[2c]

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian XL-100 spectrometer. Me_4Si was used as an internal reference. The line frequencies were measured with an electronic counter (±0.1 Hz). Mass spectra were obtained with a Varian MAT 711 spectrometer operating at an ionization voltage of 75 eV and a source temperature of 180 °C.

THS was synthesized and purified by the procedure described by McCullough and Lefohn[7] using Merck products: mass spectrum, m/e (rel intensity) 138 (6), 137 (2), 136 (38), 135 (3), 134 (18), 133 (8),)132 (7), 110 (2), 109 (1), 108 (12), 107 (5), 106 (6), 105 (4), 104 (3), 96 (4), 95 (4), 94 (22), 93 (6), 92 (11), 91 (6), 90 (5), 82 (1.6), 81 (1.6), 80 (2.4), 79 (0.9), 78 (1.3), 77 (0.5), 76 (0.4), 55 (100).

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Registry No. Cyclopentane, 287-92-3; tetrahydrofuran, 109-99-9; tetrahydrothiophene, 110-01-0; tetrahydroselenophene, 3465-98-3; cyclopentanone, 120-92-3; tetrahydrothiophene 1,1-dioxide, 126-33-0.

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(1) E. T. Strom, B. S. Snowden, Jr., H. C. Custard, D. E. Woessner, and J. R. Norton, *J. Org. Chem.*, **33**, 2555 (1968).

(2) (a) E. Diez, A. L. Esteban, and M. Rico, *J. Magn. Reson.*, **16**, 136 (1974); (b) A. L. Esteban, Ph.D. Thesis, Universidad Complutense, Madrid, Spain, 1976; (c) A. L. Esteban and E. Diez, *J. Magn. Reson.*, in press.

(3) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, CA, 1963.

(4) (a) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 2118 (1968); (b) J. A. Greenhouse and H. L. Strauss, *ibid.*, **50**, 124 (1969); (c) D. W. Wertz, *ibid.*, **51**, 2133 (1969); (d) W. H. Green, A. B. Harvey, and J. A. Greenhouse, *ibid.*, **54**, 850 (1971).

(5) (a) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.*, **92**, 5013 (1970); (b) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969); (c) A. Almenningen, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, **23**, 2748 (1969); (d) Z. Nahlovska, B. Nahlovsky, and H. M. Seip, *ibid.*, **23**, 3534 (1969); (e) *ibid.*, **24**, 1903 (1970); (f) H. J. Geise and F. C. Mijlhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 577 (1971).

(6) (a) R. L. Lipnick, *J. Mol. Struct.*, **21**, 411 (1974); (b) J. B. Lambert, J. J. Papay, S. A. Khan, K. A. Kappavf, and E. S. Magyar, *J. Am. Chem. Soc.*, **96**, 6112 (1974).

(7) J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

Organic Photochemistry with 6.7-eV Photons: Decomposition of *cis*- and *trans*-1,2-Diethylcyclopropanes, 1,1,2-Trimethylcyclopropane, and 1,1,2,2-Tetramethylcyclopropane

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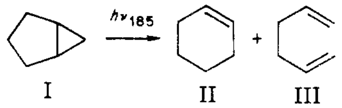
Recent work from this laboratory[1] has shown that bicyclic hydrocarbons such as I which incorporate a cyclopropane ring, on irradiation in pentane solution at 185 nm (≡6.7 eV), decompose according to eq 1 to give products



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which formally correspond to the cleavage of one or two bonds of the cyclopropane ring. These reactions are believed to occur from an electronically excited singlet state of the cyclopropane ring. Although the two-bond cleavage of cyclopropanes in gas-phase photolysis at wavelengths <185 nm is well-documented,[2] only a single example[3] of a disubstituted cyclopropane which is capable of giving stereochemical information on the photoprocess has hitherto been reported. This work will be referred to later.

The present work was intended to answer questions posed by our earlier report, which were: (i) is an alternative

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(1) R. Srinivasan and J. A. Ors. *J. Am. Chem. Soc.*, **100**, 7089 (1978).

(2) C. L. Currie, H. Okabe, and J. R. McNesby, *J. Phys. Chem.*, **67**, 1494 (1963); K. L. Hill and R. D. Doepker, *ibid.* **76**, 3153 (1972); E. Lopez and R. D. Doepker, *ibid.*, **82**, 753 (1978); A. A. Scala and P. Ausloos, *J. Chem. Phys.*, **49**, 2282 (1968); K. Shibuya, K. Obi and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1974 (1975).

(3) J. H. Vorachek and R. D. Koob, *J. Phys. Chem.*, **76**, 9 (1972); K. Dees and R. D. Koob, *ibid.*, **77**, 759 (1973).