Table I
Normal Modes of Vibration (cm^{-1}) of CO_2, HCN, H_2O, and CH_3CH_2Cl

molecule	mode	obsd	WDC[a]	SAP[b]	WDC–SAP diff, %
CO_2	bend	667.30[c]	667.45	667.29	0.024
	sym str	1337.00	1234.85[d]	1234.09[e]	0.062
	asym str	2349.35	2364.56	2363.97	0.025
HCN	bend	712.10[f]	712.30	712.34	−0.006
	sym str	2096.68	2096.64	2096.28	0.017
	asym str	3311.40	3311.40	3311.71	−0.009
H_2O	bend	1595.0[g]	1594.76	1594.67	0.006
	sym str	3651.7	3677.13	3676.98	0.004
	asym str	3755.8	3731.66	3731.43	0.006
CH_3CH_2Cl	bend	335[h]	334.18[i]	333.93[i]	0.075
	sym str	655	654.88	654.38	0.076
	asym str	966	965.90	964.94	0.099

[a] QCPE 342. [b] SAP IV. [c] From ref 11. [d] Inclusion of an off-diagonal force constant gives 1337.06 cm^{-1}. [e] Inclusion of an equivalent off-diagonal force constant parameter gives 1336.27 cm^{-1}. [f] From ref 12. [g] From ref 7. [h] From ref 14. [i] Methyl and methylene groups treated as point masses.

a linear, symmetric triatomic; HCN, a linear, unsymmetric triatomic; H_2O, a bent, symmetric triatomic; and CH_3CH_2Cl, a bent, unsymmetric pseudotriatomic. With appropriate experimental data,[7,11-14] the normal modes obtained are those shown in Table I.[15,16] As can be seen, comparable pairs of values match well.

Validity of SAP IV *for Static Molecular Analysis.* Since the equations used in the beam–FEM technique for static analysis are a subset of the equations used for dynamic analysis, the beam–FEM technique is valid for the static analysis of triatomics as well. Further consideration shows that it is also valid for the static analysis of other molecules whose frameworks can be constructed of overlapping triatomic segments. This includes many crystal lattices, tube polymers, and other similar, inherently stiff molecular frameworks. For frameworks that cannot be constructed of overlapping sets of triatomics, additional beams can be introduced to give frameworks that are composed of overlapping triatomics. These additional beams can be assigned properties such that they correctly reproduce the behavior of the frameworks of interest.[18] In this manner the static and dynamic analysis of all molecular frameworks is possible. Thus the beam–FEM technique permits types of analysis that are not presently possible with the molecular modeling systems commonly available.

Acknowledgment. We thank James T. Kenney, Jr., and John G. Kenney of Project Engineering Co. and Robert C. Hedricks of the Lewis Research Center of NASA for helpful conversations. We also thank Celanese Research Co. for financial support.

Registry No. CO_2, 124-38-9; HCN, 74-90-8; H_2O, 7732-18-5; H_3CCH_2Cl, 75-00-3.

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(15) Minor modifications were made in SAP IV for all four sets of calculations. These included altering the units of the input parameters to alleviate overflow problems and altering the output format to permit the program to be interfaced with molecular graphics programs.
(16) For the calculations on CO_2 and H_2O the eigensolver of SAP IV was also replaced. This was done because the original eigensolver sometimes terminates its search for the desired eigenvalues before finding all of them. The replacement routine,[17] while more cumbersome, consistently solves for all the desired values of these molecules. This routine was not used for HCN and CH_3CH_2Cl because the original routine solves for the desired values efficiently and because it is known to solve for the lowest eigenvalues of large, complex structures efficiently.
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Received March 17, 1986

Photoresponsive Polymers. Reversible Bending of Rod-Shaped Acrylamide Gels in an Electric Field

An attempt to use photochemical reactions of photochromic compounds at the molecular level for direct conversion of photon energy into mechanical work was initiated by Merian.[1] The system studied by Merian was nylon filament fabric, 6 cm wide and 30 cm long, containing 15 mg/g of azo dye. After exposure to a xenon lamp, the dyed fabric was found to be 0.33 mm shorter. Since then, many materials, most of which contained azobenzene chromophores in polymers, have been reported to show photostimulated deformation.[2] Till now, however, the reported deformations were limited to less than 10%.

We report here photostimulated reversible bending of rod-shaped polyacrylamide gels having triphenylmethane leucocyanides in an electric field. In previous reports,[3] it was shown that the size of the gel having 3.1 mol % leucocyanide groups increased by as much as 120% in each dimension upon ultraviolet irradiation ($\lambda > 270$ nm). The dilated gel shrank in the dark to its initial size. The driving force of the gel expansion is an osmotic pressure differential between the gel inside and the outer solution, which is produced as a result of the photodissociation of the leucocyanide groups attached to the gel network. During the course of experiments to reveal an electric field effect on the behavior of the mobile CN^- ions in the gels, we found a peculiar behavior of the gel, reversible bending of the gel.

Rod-shaped acrylamide gels containing triphenylmethane leucocyanide groups (25 mm in length and 2 mm

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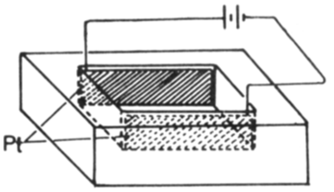

Figure 1. Sketch of the water pool used for measurement.

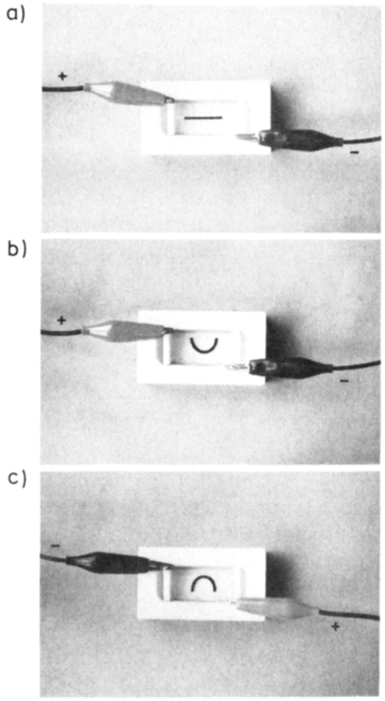

Figure 2. Photostimulated bending of a rod-shaped acrylamide gel (25 mm in length and 2 mm in section diameter) having 3.1 mol % triphenylmethane leucocyanide groups in an electric field (10 V/cm) in water (pH 6.5): (a) before photoirradiation; (b) under ultraviolet irradiation ($\lambda > 270$ nm); (c) under ultraviolet irradiation ($\lambda > 270$ nm) (the polarity of the electric field was opposite to that in (b)).

in section diameter) were prepared in capillary tubes by free radical copolymerization of acrylamide and bis(*N*,*N*-dimethylanilino)(4-vinylphenyl)methane leucocyanide in dimethyl sulfoxide (Me_2SO) in the presence of *N*,*N*-methylenebis(acrylamide).[3] The gels were removed from the capillary tubes and soaked in Me_2SO and then in water to remove all residual monomers and initiators.

The gels were swollen to the equilibrium condition on standing in water overnight. Then the gel was placed in a small water pool (Teflon, 36 × 19 × 15 mm) with two parallel platinum electrodes as schematically shown in Figure 1.

Figure 2 shows photostimulated bending of an acrylamide gel having 3.1 mol % triphenylmethane leucocyanide groups in water (pH 6.5) in an electric field. In the dark, the gel shape did not change in a 10 V/cm electric field (Figure 2a). Upon ultraviolet irradiation ($\lambda > 270$ nm), the gel quickly bent in 1 min. The gel ends moved toward the positive electrode as shown in Figure 2b. During the bending, the center of gravity of the gel remained at the initial position. Translational motion of the entire gel to the negative electrode was not observed.

When the polarity of the electric field was changed, the gel again became straight and then bent in the opposite direction (Figure 2c). The response time of the gel shape change was around 2 min. The bending of the gel in response to the changes of the polarity could be repeated many times under ultraviolet irradiation. After the light was switched off, the gel slowly returned to the initial straight shape in the electric field. This result suggests that photodissociation of the leucocyanide groups in the gel is indispensable to the gel bending motion.

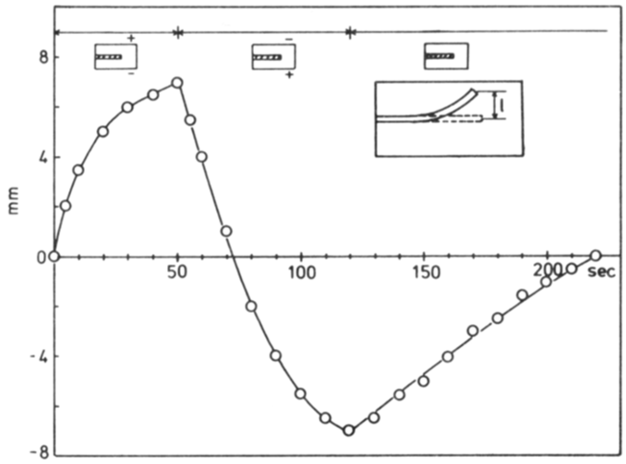

Figure 3. Photostimulated bending of a rod-shaped acrylamide gel (26 mm in length and 2 mm in section diameter) having 3.1 mol % triphenylmethane leucocyanide groups in an electric field (10 V/cm) in water (pH 6.5). The electric field was removed after 120 s.

In order to determine quantitatively the response time of the motion, one end of the rod-shaped gel was fixed to the wall and the distance that the free end moved from the initial position (*l*) was measured as a function of irradiation time. Figure 3 shows the photostimulated bending motion of the gel (26 mm in length and 2 mm in section diameter) in an electric field (10 V/cm). The free end moved toward the positive electrode with an initial speed of 0.40 mm/s. When the polarity of the electric field was changed, the end moved in the opposite direction. When the electric field was switched off, the bent gel returned to the initial position with a speed of 0.075 mm/s. Although the speed of bending became very slow, bending was observed under a very weak electric field of 1.25 V/cm. In this case, the effective voltage applied to the gel was only 0.25 V.

The bending behavior of the gel suggests inhomogeneous expansion of the gel in the electric field. The negative electrode side of the gel expands to a greater extent than the positive electrode side. Since the electric field is applied perpendicular to the gel axis, mobile negative CN^- ions are attracted to the positive electrode side in the gel. Consequently, excess positive charges are left on the other side. Internal repulsive force between the positive charges, which are fixed in the gel network, is considered to cause the expansion of the negative electrode side of the gel.

Under dark conditions, polyelectrolyte gels have been reported to shrink in an electric field. In contrast to the present system, the gels are in contact with electrodes in these experiments. One example is polyacrylamide gels having acrylic acid groups.[4] The contraction behavior was accounted for by analyzing the minimization conditions of the total free energy, the free energy associated with the deformation of the gel, and the energy associated with the work done by the negatively charged acrylic acid groups in the electric field. The absence of translational motion and the quick response in the present system suggest that such an external force on the fixed positive charged groups to pull the gel toward the negative electrode plays a minor role in the gel bending motion.

The deswelling of gels under an electric field was also reported for a water-swollen poly(2-acrylamido-2-

methyl-1-propanesulfonic acid).[5] The contraction of the gel was interpreted as follows. Under an applied electric field, the charged polymer network migrates to the positive electrode and is adsorbed to the electrode surface, losing hydration power due to the neutralization of the macrocharges. This mechanism cannot be applied to the present system, because our gel does not attach to the electrodes.

The photomechanical effect under the electric field has a variety of potential applications for sensors, switches, and photomechanical transducers.

Acknowledgment. The author thanks D. Kungwatchakun for her assistance in this study.

Registry No. (Acrylamide)(bis(*N*,*N*-dimethylanilino)(4-vinylphenyl)methane)(*N*,*N*-methylenebis(acrylamide)) (terpolymer), 94352-06-4.

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Received June 26, 1986

CORRECTIONS

Frank S. Bates* and Mark A. Hartney: Block Copolymers near the Microphase Separation Transition. 3. Small-Angle Neutron Scattering Study of the Homogeneous Melt State. Volume 18, Number 12, December 1985, p 2478.

We inadvertently used the same notation (k) in two distinct instances in the Appendix. This is rectified by exchanging l for k in the original definition of the Schulz–Zimm distribution. There were also several typographical errors, which are corrected as follows:

$$\theta(n) = (l/n_{\mathrm{N}})^{l+1}n^{l}\exp[-(l/n_{\mathrm{N}})n]/\Gamma(l+1) \quad \text{(A-3)}$$

where $l = [(n_{\mathrm{W}}/n_{\mathrm{N}}) - 1]^{-1}$

$$\overline{Ng_1(\Phi)} = \int_0^\infty\int_0^\infty \theta(N_1)\theta(N_2)\frac{2}{y^2} \times \left[\Phi y + \frac{1}{N}\exp(-\Phi N y) - \frac{1}{N}\right] \mathrm{d}N_2\,\mathrm{d}N_1 \quad \text{(A-4)}$$

$$\overline{Ng_1(1-\Phi)} = \frac{2\bar{N}}{x^2}\left\{\frac{x}{2}F(1,k+1;2k+3;z) + \frac{1}{(1-\Phi)(3-\lambda)}[(1+(1-\Phi)x(\lambda-1))^{-k}F(1,k+1;2k+2;z'') - F(k+1,1;2k+2;z)]\right\} \quad \text{(A-6)}$$

where $x = q^2\bar{R}^2 = q^2\bar{N}a^2/6$.

These corrections do not affect any of the calculations, figures, or conclusions of the paper.

Daniel R. Coulter,* Amitava Gupta,* Andre Yavrouian, Gary W. Scott, Donald O'Conner, Otto Vogl, and S.-C. Li: Electronic Energy Transfer and Quenching in Copolymers of Styrene and 2-(2′-Hydroxy-5′-vinylphenyl)-2*H*-benzotriazole: Photochemical Processes in Polymeric Systems. 10. Volume 19, Number 4, April 1986, p 1227.

Equation 3 on p 1231 should read

$$(R_0)^6 = \frac{9000\Phi_{\mathrm{D}}k^2 \ln 10}{128\pi^5 n^4 N}\int F_{\mathrm{D}}(\bar{\nu})\epsilon_{\mathrm{Q}}(\bar{\nu})\frac{\mathrm{d}\bar{\nu}}{\bar{\nu}^4}$$

Equation 5 on p 1233 should read

$$C_{\mathrm{E}} = C_{\mathrm{HPB}}\left(\frac{R_0{}^{\mathrm{HPB}}}{R_0{}^{\mathrm{E}}}\right)^3$$