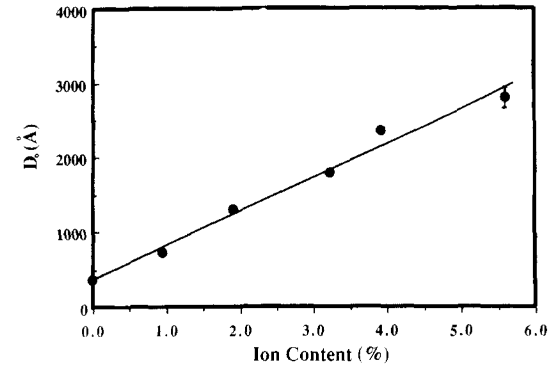

Figure 2. Plots of effective diameter at zero concentration, D_0, against ion content for S-xSSA-Na in DMF.

range Coulombic interaction and nonrandom arrangement (ordering) of macroions:

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)}\left\{1 + \frac{2B'}{M}c\Phi(hD)\right\} \qquad (1)$$

where $\Phi(x) = (3/x^3)(\sin x - x\cos x)$, $h = (4\pi/\lambda')\sin(\theta/2)$, and $B' = (2\pi/3)D^3N_0$. Also, $P(\theta)$ represents the particle scattering factor, λ' the wavelength of light in the medium, θ the scattering angle, and N_0 Avogadro's number. Here, D is the effective ionic diameter of macroions, which is a decreasing function of concentration.

As a first step of an analysis, we analyzed the initial slope of the Kc/R_0 vs. c curve. From the above equation, the initial slope is obtained as

$$\text{initial slope} = \left[\frac{\mathrm{d}}{\mathrm{d}c}\left(\frac{Kc}{R_0}\right)\right]_{c=0} = \frac{4\pi N_0}{3M^2}{D_0}^3 \qquad (2)$$

here, D_0 represents the effective diameter of a macroion at zero polymer concentration. We also used the relations $P(0) = 1$ and $\Phi(0) = 1$. By using eq 2, we calculated the effective diameters from the initial slopes, which were obtained by curve fitting of a third-degree polynomial.

The effective diameters at zero concentration are plotted as a function of ion content in Figure 2. It is seen that D_0 is a linear function of ion content. The effective diameter is a measure of distance of closest approach of centers of macroions and therefore reflects the range of interaction of macroions with other macroions.[16] The large change in effective diameter with ion content—for example, at 4% ion content, D_0 increases to 2200 Å from 420 Å for PS—is consistent with the observed large change in viscosity.[5]

In summary, polyelectrolyte behavior was studied by using ionomers in a polar solvent. Light scattering data show that the polyelectrolyte behavior is enhanced with increasing ion content. It is found that the effective diameter of ionomers increases linearly with ion content at least up to the 5% ion content level. More detailed experiments and analysis of the light scattering data are under way and will be reported.

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A Finite Element Method for Determining the Stiffnesses of Tube-Polymer Frameworks

In earlier papers a discussion of known and potential inorganic and organic polymers with tube frameworks has been given, Figure 1.[1-3] Many of these very unusual polymers have frameworks with linkage arrangements that lead to inherent stiffness. Some of the frameworks, because of the details of their linkage arrangements, are connsiderably stiffer than others.

In view of the probable importance of tube polymers and the novel and substantial differences in the stiffnesses of their frameworks, it is desirable to have a technique suitable for quantitatively determining these stiffnesses. However, no such technique has been described. Our interest in having such a technique has led us to investigate the methods used in engineering to determine the stiffnesses of trusses and other large, complex structures.

One method currently used for this purpose is the finite element method.[4] In this method, the properties of a structure are represented by the properties of a set of structural elements (e.g., a set of pipes, I-beams, or blocks), and the properties of these are appropriately summed to determine the global behavior of the structure. Since in many cases this method requires considerable computation, it is commonly carried out with the aid of an appropriate program.

One such program is SAP IV.[5] This is an established program that can be applied to structures whose complexity and size require models having not only several types of elements but also thousands of them.[6] The program can be used for the static analysis of structures and

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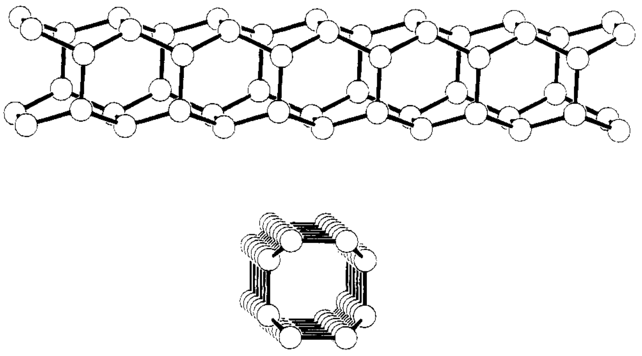

Figure 1. Side and end view of the framework of a hypothetical tubular polymer that, because of its linkage arrangement, is relatively stiff.

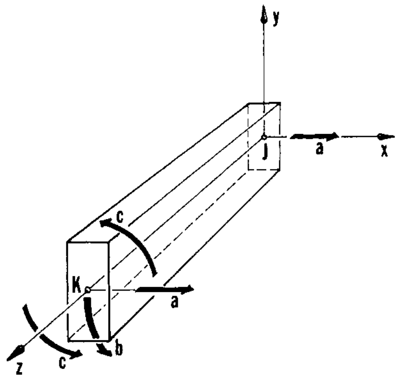

Figure 2. A beam between nodes *J* and *K* showing three of its six possible degrees of freedom: (a) displacement along *x*; (b) bending about *x* with node *J* fixed; (c) torsion about *z* with node *J* fixed.

thus, as indicated, for the calculation of their global stiffness properties. It can also be used for the dynamic analysis of structures and hence for the calculation of their vibrational frequencies.

Among the various types of elements that are used in the finite element method is a beam with six degrees of freedom (independent motions). If the long axis of this beam element is taken as the *z* axis, these six degrees of freedom consist of three displacement degrees along the *x*, *y*, and *z* axes, two bending degrees about the *x* and *y* axes, and one torsional degree about the *z* axis, Figure 2.

This beam element allows properties to be included in the analysis of a structure that are analogous to those included in the analysis of a molecule when the molecule is represented with a valence force field model. (This model assumes that the fundamental vibrations of a molecule are controlled by bond stretching and bond angle bending and neglects the influences of nonbonded interactions.[7])[8]

Accordingly, a technique for the static and dynamic analysis of molecules can be postulated in which the bonds and atoms of a molecule are represented with beams and nodes, and the resulting model is analyzed by the finite element method using SAP IV. This technique, the beam–FEM technique, is a candidate for calculating the stiffnesses of tube-polymer frameworks.

A proof that the beam–FEM technique is valid for tube-stiffness calculations can be started by showing that when it is used for determining the normal modes of triatomics, it is equivalent to a common, conventional technique for this purpose. In this latter technique, a molecule is represented with a valence force field model and the model is analyzed by the method of Wilson, Decius, and Cross.[9] (In Wilson's method an approximate potential function for a molecule in terms of internal coordinates is devised and this is used as a basis for calculating the normal modes.)

Equivalence of Techniques. The equivalency of the two techniques can be shown by beginning with the equation for the square of the bending frequency of an unsymmetric triatomic molecule in radians/second, ω^2, in the conventional (Wilson) technique and the corresponding equation in the beam–FEM technique. The first equation is

$$\omega^2 = K_b\{[L_1{}^2/M_3] + [(L_1 + L_2)^2/M_2] + [L_2{}^2/M_1]\}/L_1{}^2L_2{}^2 \quad (1)$$

where *L* is the length of a bond, *M* is the mass of an atom, and K_b is the bending force constant. The corresponding equation in the beam–FEM technique is

$$\omega^2 = [3E_1E_2I_1I_2L_2{}^2M_2M_3 + 3E_1E_2I_1I_2L_2{}^2M_1M_3 + 6E_1E_2I_1I_2L_1L_2M_1M_3 + 3E_1E_2I_1I_2L_1{}^2M_1M_3 + 3E_1E_2I_1I_2L_1{}^2M_1M_2][(E_1I_1L_1{}^2L_2{}^3 + E_2I_2L_1{}^3L_2{}^2)M_1M_2M_3]^{-1} \quad (2)$$

where *E* is the Young's modulus of a beam (bond), *I* is a moment of inertia of a beam about its *x* and *y* axes, and *M* is the mass of the node (atom). (This equation is derived from the equations of motion in SAP IV by transforming these equations from matrix form to algebraic form and solving them for ω^2.[10])

Equating expressions 1 and 2 and solving for K_b give

$$K_b = 3E_1E_2I_1I_2/(E_1I_1L_2 + E_2I_2L_1) \quad (3)$$

Since this relationship can be satisfied independently of the mass and the specific geometry of the molecule, the two techniques describe the bending response of triatomics identically.

Equating the expressions for the square of the stretching frequency in the two techniques and solving for the stretching force constant, K_s, give

$$K_s = EA/L \quad (4)$$

where *A* is the cross-sectional area of the beam. Again this relationship is independent of mass and geometry. This shows that the two techniques also describe the stretching response equivalently. Hence, the beam–FEM technique correctly gives the dynamic response of triatomics.

Implementation of SAP IV. Since more parameters are used to describe bending and stretching in the beam–FEM technique than in the conventional technique, it can be assumed without a loss in the ability of a beam element to represent a bond that

$$A = 1 \quad (5)$$

and that

$$I_1 = I_2 = I' \quad (6)$$

From these equations it follows that

$$E = K_sL \quad (7)$$

and

$$I' = K_b(E_1L_2 + E_2L_1)/3E_1E_2 \quad (8)$$

With eq 7 and 8, the normal modes of triatomics can be obtained with the beam–FEM technique using conventional force constants.

Demonstration of Equivalency. To demonstrate their equivalency for the vibrational analysis of triatomic and pseudotriatomic molecules, the two techniques were used to analyze four molecules. For this work QCPE 342,[11] a readily available program based on Wilson's method, was employed. The molecules that were examined are CO_2,

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.

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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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(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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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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