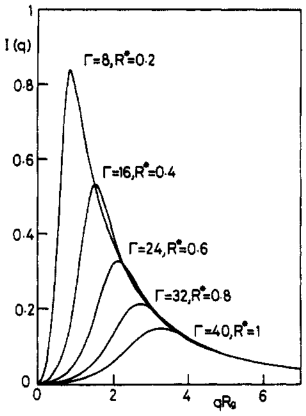

Figure 1. The scattering intensity (in arbitrary units) from a solution of polyelectrolyte chains in the form of Gaussian coils (with radius of gyration R_g) for different chain concentrations. The polyion charge is fixed with $\Gamma/R^* = 40$, and curves labeled by smaller Γ (or lower R^*) values correspond to more dilute solutions.

molecules. In this Note we present a generalization of this model that is, in principle, applicable to solutions of both spherical and rodlike polyelectrolyte chains at any concentration.

The scattering intensity $I(q)$ for a one-component system may be written

$$I(q) \propto P(q)S(q) \qquad (1)$$

where $P(q)$ is the intrachain structure factor or form factor, $S(q)$ is the interchain structure factor, and the wavevector $q = (4\pi\lambda^{-1}) \sin (\theta/2)$ (λ being the wavelength of the incident radiation and θ the scattering angle). The structure factor may also be expressed in terms of the Fourier transform of the direct correlation function $C(q)$, which is defined by

$$S(q) = (1 - nC(q))^{-1} \qquad (2)$$

where n is the number density of chains.[2] The present model consists of using the single-contact approximation[3] to express $C(q)$ as a product of the form factor $P(q)$ and an interchain monomer–monomer interaction factor, which for uncharged macromolecules is known as the excluded volume parameter ν.[4] However, for polyelectrolytes the range of interaction may be large due to the screened Coulomb interaction between charged monomers and ν becomes q-dependent. This represents a direct correlation between monomers on different chains which is denoted $C_m(q)$ and allows us to write

$$C(q) = C_m(q)P(q) \qquad (3)$$

Hence we find from eq 1–3

$$I(q) \propto \frac{P(q)}{1 - nC_m(q)P(q)} \qquad (4)$$

In the absence of added salt, when screening effects are small, the effective monomer–monomer direct correlation function $C_m(q)$ should be well represented by a one-component plasma (OCP) for all but very small wavevectors,[5] the OCP being a one-component fluid of charged point particles interacting through an unscreened Coulomb potential where the counterions form a uniform neutralizing background.[6]

To illustrate this result, Figure 1 shows the scattering intensity for a solution of polyelectrolyte chains in the form of Gaussian coils where a Debye function may be used for $P(q)$ with

$$P(q) = 2u^{-2} (\exp(-u) + u - 1), \qquad u^{1/2} = qR_g \qquad (5)$$

and R_g is the radius of gyration of the coil.[7] $I(q)$ is plotted for several values of the OCP coupling constant Γ[6] and ratio $R^* = R_g/a$ such that Γ/R^* is fixed ($a = (3/4\pi n)^{1/3}$ is the ion sphere radius for the polyion and typically $R^* \lesssim 1$). This corresponds to variations in the number density n for fixed values of the polyion charge, with smaller Γ (or lower R^*) values representing more dilute solutions. Figure 1 reproduces correctly the qualitative behavior of the experimental data reported by Nierlich et al.[8] and Matsuoka et al.[9] for the scattering intensity as a function of polyelectrolyte concentration for both biopolymers and synthetic polyelectrolytes.

It is relatively simple to fit the experimental and theoretical results by adjusting the apparent charge on the polyion, which is unknown due to the counterion condensation that may occur in such systems, and using an appropriate choice for the form factor $P(q)$.

The unphysical feature of Figure 1 occurs in the $q \to 0$ limit, when the OCP model requires $S(q) \to 0$ as $q \to 0$.[6] However this feature is removed by the inclusion of screening effects from the counterions, which in such systems represents a small perturbation and affects the scattering at only very small wavevectors.[5]

A more elaborate study of this model along with its generalization to multicomponent systems is in progress and will be reported later.

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Phase Transitions in Cross-Linked Gels of Natural Polymers

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Some synthetic polymer gels were reported to undergo discontinuous volume phase transitions in response to infinitesimal changes in temperature,[1] solvent composition,[2-5] pH,[6] ionic composition,[6] or by application of a small electric field across the gel.[7] It has also been suggested theoretically that the phenomena are similar to the gas–liquid phase transition, where the reversible volume changes up to a couple of thousand times have been observed upon temperature change.[2] It has further been shown theoretically that for a gel to undergo a discontin-

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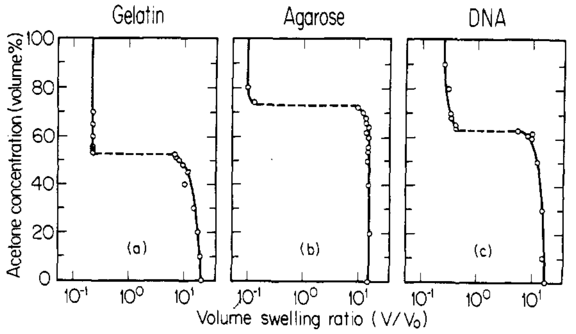

Figure 1. (a) Equilibrium volume of a gelatin gel, chemically cross-linked by ethylene glycol diglycidyl ether, shows a discontinuous change in acetone–water mixtures when the mixture composition is varied. At lower acetone concentrations the gel is swollen, whereas at higher concentrations the gel is collapsed. A discontinuous volume transition occurs at 53%. (b) Agarose gels, cross-linked by ethylene glycol diglycidyl ether, also undergo a discontinuous volume transition in acetone–water mixtures. The polymer network is ionized by chemically substituting its hydroxy groups with glycidyltrimethylammonium chloride. At lower acetone concentrations the gel is swollen, whereas at higher concentrations the gel is collapsed. The discontinuous volume transition occurs at 72%. (c) DNA gels undergo phase transition. The transition acetone concentration is about 63%, and the volume change is 15 times.

uous volume phase transition the gel should be subject to a sufficiently large internal osmotic pressure (or equivalently, negative external osmotic pressure) and that the solvent in which the gel is immersed should be sufficiently poor.[2,8] An adequately poor solvent can be readily found for any polymer network. A positive internal osmotic pressure can be created by ionizing the polymer network; the pressure originates from the translational degrees of freedom of the counterions trapped inside the gel surrounded by the Donnan potential wall.[2]

The universality of the phase transition in any gel and the criterion for a discontinuous volume transition in gels are analogous to the situation for the gas–liquid phase transition. Recall that the gas–liquid transition, such as evaporation and condensation of water, is a universal phenomenon common to all materials. It is also known that the gas–liquid volume change is discontinuous if the pressure is low but continuous if it is high, as shown by the van der Waals equation of state. A similar situation exists for the polymer network of a gel immersed in a fluid.

Experiments support the universal feature of the phase transition in polymer gels.[1-7] However, the gels that have been found to exhibit discontinuous volume transitions so far are all synthetic polymers such as acrylamide (and its derivatives)/acrylic acid copolymer gels and sulfonated styrene gels. They are all polyvinyl compounds. The question remains whether the phase transition is universal for all gels. Is it true for gels of polymers having chemical bonds and conformations different from synthetic vinyl polymers? Particularly interesting are gels made of natural polymers. They are polymerized by peptide bonds (proteins), phosphate ester bonds (DNA), and ether bonds (polysaccharides). A discontinuous, reversible volume transition in natural gels would also have substantial importance from the medical and technological point of view.

In this letter we present observations of a discontinuous phase transition in gels made of the three kinds of natural polymers: DNA (polynucleotide), gelatin (polypeptide), and agarose (polysaccharide). These observations strongly support the theoretical prediction that the phase transition of gels is universal and should not be confined to a specific group of gels.

Gelatin polymer (Atlantic Gelatin General Food Corp., hard capsule 203B) in water (10%) is chemically cross-linked by using ethylene glycol diglycidyl ether (EGDE) in the amount of 10% of gelatin polymer at 60 °C, pH 11, for 15 h. DNA (Sigma, type III sodium salt from salmon tests) in water (20%) is cross-linked by using EGDE (50% of DNA) at pH 11, 55 °C, for 3 h. Agarose polymer (Bethesda Research Laboratories, LAP agarose) in water (5%) is cross-linked by EGDE (10% of agarose) at pH 11.5, 75 °C, for 20 h. All gelations are carried out in cylindrical micropipets of 1.35-mm i.d. (d_0). The polymer network of agarose is ionized by chemically substituting its hydroxy groups with glycidyltrimethylammonium chloride (GMAC). The reaction takes place in 2% GMAC aqueous solution at pH 11.5, 60 °C, for 20 h. Since DNA and gelatin polymers are naturally ionized, incorporation of ionizable groups are not necessary. Gels of known diameters are placed in sealed acetone–water mixtures of various compositions. After the gels reach equilibrium the diameter of the gels is measured under the calibrated microscope. From the diameter (d), we determine the degree of swelling $V/V_0 = (d/d_0)^3$, where V and V_0 are the final and initial volumes of gels, respectively.

The cross-linked gelatin gel is swollen in water. As acetone is added to water the gel shrinks but only slightly. At 53% acetone composition the gel suddenly shrinks by 50 times. The volume change is discontinuous. The transition is reversible; when water is gradually added to the solution containing a collapsed gelatin gel, the gel reswells at 53% acetone. Similar discontinuous transitions are observed in the DNA and ionized agarose gel. The volume changes at the transitions are 15 times for the DNA gel and 100 times for agarose gel. The transition acetone concentrations are 63% for DNA and 72% for agarose gels.

We have some evidence that with the increase of ionization of the polymer network, the volume change at the transition becomes larger, as expected from theoretical considerations.[2]

The experiments presented here clearly demonstrate the universality of phase transitions in polymer gels. Zimm and colleagues found that DNA indeed undergoes a very sharp volume transition when pH is varied.[10]

The concept and the knowledge of the phase transition in natural gels will also be an invaluable guiding principle in developing artificial muscles and organs, drug delivery systems and storable foods. The biogels will be used to pump and harvest bioproducts by absorbing the solvent containing the bioproducts and then by squeezing out the solvent.

In addition to its technological importance, the finding of phase transitions in the gels of natural polymers opens a door to a wide variety of interesting experiments. For example, both agarose and gelatin polymers undergo a gel–sol transition: At high temperatures they are in solution form, but at lower temperatures they become gels due to a weak physical bond (in contrast to the chemical, permanent cross-links introduced in our experiments). The coupling of gel–gel phase transition and internal gel–sol transition is an interesting subject to explore. Natural polymers also undergo several different types of helix–coil transitions. Again, the coupling of these transitions to the ones mentioned above in very interesting.

Though acetone–water mixtures were used in our experiments, other solvent mixtures such as alcohol–water will also be used to demonstrate the phase transition. At appropriate solvent compositions, the temperature, ionic composition, and pH will induce the phase transition as shown in synthetic polymer gels.

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Communications to the Editor

Starburst Dendrimers. 4. Covalently Fixed Unimolecular Assemblages Reminiscent of Spheroidal Micelles

It has been stated that aqueous micelles are "stable, disjoint, cooperative, closed equilibrium colloidal aggregates"[1] that possess topological order (an inside and an outside) and may be more accurately thought of as dimensionally discordant fractals.[2,3] A variety of ingenious models has been proposed to explain certain of these aggregate structures, and they include those proposed by Menger,[4] Franses,[1] Hartley,[6] Wennerström and Lindman,[7] Ninham,[8] Butcher[2] and Dill,[5] to mention a few. "Unfortunately, there is no direct method available to date for unequivocal determination of micellar structures",[9] although it is known that micellar size, shape[10] and structure[11,12] can dramatically affect the kinetics and course of reactions occurring in these microdomains. Currently, there is some controversy over micellar structure[13] and possible perturbation effects caused by introduction of probe (guest) molecules into these aggregates. For this reason, it would be of interest to mimic the fundamental parameters (i.e., size, shape, topology, and chemical functionality) associated with these microenvironments in a "covalently fixed" model. In our quest for such models, we examined molecular architecture possessing regular dendritic branching with radial symmetry, which we refer to as "starburst dendrimers". Their successful synthesis and characterization has allowed us to demonstrate the *controlled occupation of microspace in three dimensions as a function of size, shape, and disposition of desired organic functionality.*[14] More recently, Newkome and co-workers[15] have reported related "treelike" structures called arborols and compared them to micellar organizations, albeit without size or shape documentation. In this Communication, we wish to compare the properties of a series of starburst dendrimers (poly(amido amines)) with important spheroidal micelle criteria to see if they are consistent with such parameters as size, shape, quantization of head groups (aggregation number), head-group functionality, and topology.

Examples of covalently fixing (stabilizing) aqueous micelles into nonequilibrating unimolecular assemblies remains rare[16] if not uncertain at this time.[17] Unlike micelles, related assemblages such as liposomes (vesicles) have been successfully stabilized by polymerization[18] of unsaturated amphiphiles to produce a wide variety of "membrane mimetic" systems.[9]

A series of three directional dendrimers [A-E, core, NH_3; repeating unit, $-CH_2CH_2C(O)NHCH_2CH_2N-$; Z = $-CO_2Me$ or $-NH_2$] with projected two-dimensional branching patterns and empirical formula as shown in Chart I was examined. Inspection of the unimolecular dendrimer structures shows that they mimic the topology and discrete aggregation numbers noted for multimolecular micellar assemblies in that the number of dendrimer head groups (Z) is quantized as a function of generation A–E. Accumulation of Z groups per generation is equal to $N_c N_r^{G-1}$, where N_c is the multiplicity of the initiator core, N_r is the repeating unit multiplicity, and G is the generation (i.e., A $\equiv$ Gen = 2 $\rightarrow$ E $\equiv$ Gen = 6 with Z = 6 and 96, respectively, as shown in Table I).

Scaled Corey–Pauling molecular models (Figure 1) were compared to hydrodynamic solution dimensions as well as electron microscopy measurements of individual dendrimer

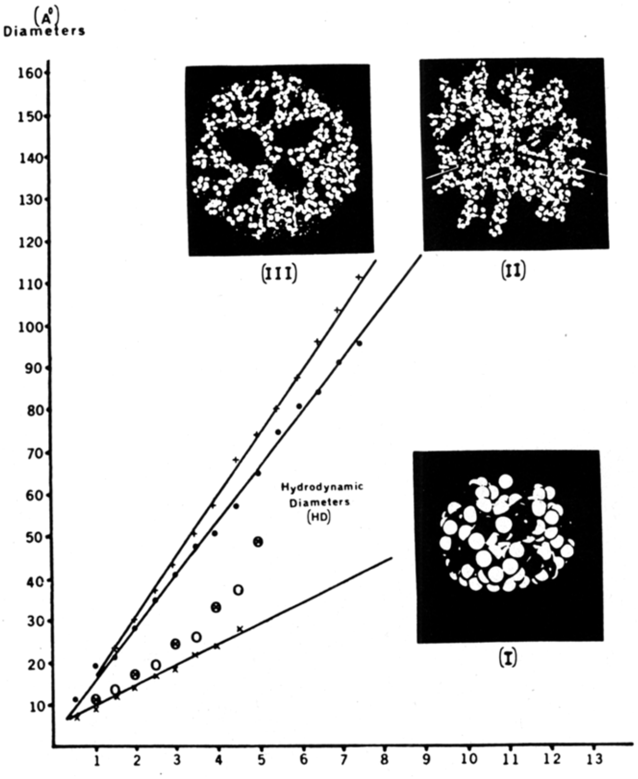

Figure 1. Comparison of starburst poly(amido amine) dendrimer hydrodynamic diameters (HD) vs. generation: (⊗) amine-terminated dendrimers, generations = 1–5; (○) carbomethoxy-terminated dendrimers, generations = 1.5–4.5. Comparison of CPK model measured diameters vs. generation: (×) form I, three-dimensional *contracted*, (●) form II, three-dimensional *extended*, (+) form III, two-dimensional *extended* (collapsed).

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