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Dynamic Mechanical Behavior of Polyelectrolyte Gels with Sulfonic Acid Groups

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Introduction

In recent years, polymeric gels were widely studied as a new material useful in many fields. The response to the macroscopic deformation is an important fundamental property characterizing the gel system with respect to molecular dynamics and mechanical performance. Many papers have been published on the mechanical behavior of nonpolyelectrolyte gels,[1] showing their rubberlike elasticity. For polyelectrolyte gels, however, there have been only a few reports about the modulus on poly(acrylic acid) and/or poly(methacrylic acid) gel samples[2-4] which were weakly charged by partial neutralization. None of these observations have shown the frequency dependence of the modulus for gels, and furthermore the swelling state would be altered for those weakly ionized gels with a change in the degree of neutralization.

Because of their network nature formed during polymerization, the elastic property of synthesized gels is usually described using the classical theory of rubber elasticity.[5,6] When there are ionized groups on the chain, however, as there is for a polyelectrolyte gel swollen in water, the electrostatic interaction makes the situation much more complicated. One can imagine that, when a macroscopic deformation acts on a polyelectrolyte gel, the spatial distribution of the distance between charges in the gel would be changed and that consequently the potential energy of the system would vary during the deformation process. Theories concerning the contribution of electrostatic interaction to elasticity are extremely limited.[7,8]

In order to investigate the dynamic mechanical behavior of polyelectrolyte gels, especially those with strong charges, we chose the network containing the monomers with sulfonic acid side groups as our sample. These samples can dissociate completely into polyanions and protons in water so as to avoid difficulty in determining the ionization degree of a sample as arising in the gels with weakly ionizable groups.[3,9] The dynamic shear modulus was determined with frequency and strain scans on samples which have different charge densities. The results are discussed in terms of the kinetic theory of rubber elasticity which has been modified using Katchalsky's random-coil model,[10] proposed by Hasa et al.,[7,8] to include the electrostatic potential change which occurs during the deformation.

Experimental Procedures

Sample Synthesis. Six gel samples were prepared by free-radical copolymerization of *N,N*-dimethylacrylamide (DMAA) and 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS), with *N,N'*-methylenebisacrylamide (BIS) as the cross-linker and ammonium persulfate (APS) as the initator. All reagents except DMAA were purchased from Wako Chemicals Co. The DMAA was purchased from Tokyo Kasei Co. The reagents were used without further purification. The water used in the synthesis was purified by a Millipore system to the resistivity of 18 MΩ cm and degassed under reduced pressure for about 90 min.

The desired amounts of DMAA, AMPS, and BIS were dissolved in water and degassed, and an aqueous solution of APS was also degassed. The two solutions were then poured together to form a pregel solution in a bag filled with nitrogen. After being uniformly mixed, the pregel solution was injected into a gap of thickness of about 3.2 mm formed between two glass plates and kept at 80 °C for about 2 h. The gel sample so prepared was then removed from the glass model and stored at 5 °C before rheological measurement.

Table I. Gel Samples with Sulfonic Acid Groups and Their G_e

sample code	f	M_0	$G_e \times 10^{-4}$ (dyn/cm^2)
DS0	0.0	99.9	5.75
DS10	0.10	110.7	6.62
DS20	0.20	121.5	8.01
DS30	0.30	132.3	5.74
DS50	0.50	153.9	4.22
DS70	0.70	175.5	1.84

The composition of the gel sample was expressed by stoichiometric amounts of the three monomers in the pregel solution. Three variables were used to define this composition:[11] (1) the total molar concentration C_t of all monomers (including BIS) in the pregel solution, which was kept at 0.75 mol/L for all samples in this study; (2) the mole fraction C of BIS in all monomers, held at 0.013 in our six samples; (3) the mole fraction f of AMPS in all monomers, which was varied from 0 to 0.70 as listed in Table I. Since sulfonic acid groups of AMPS can be ionized completely in the gel state, the change in f will alter the charge density in the sample.

Rheological Measurements. Oscillatory shear deformation on the gel samples with different f values was carried out with a Rheometrics RFS-II fluid spectrometer using parallel plates of 25.0 mm diameter. The dynamic modulus was recorded at 22 °C in a radian frequency ω range from 10^{-1} to 10^2 rad/s by consecutive frequency scans at a constant shear strain γ of 0.1% and in a γ range from 0.1% to 100% by strain scans at $\omega = 6.28$ rad/s.

Results and Discussion

Viscoelastic Behavior. The absolute values of the complex modulus G^*, dynamic storage moduli G', and loss moduli G'' of sample DS20 are shown in Figure 1. The measurements of G^* as the shear strain γ varies from 10^{-1} to 10^2% are shown in the upper panel. For these data points, a horizontal line has a very good fit, indicating that the response of the polyelectrolyte gel to the sinusoidal deformation is linear in this γ range.[12] In the lower panel, the values of G' also become a constant about equal to G^* at frequencies ranging from 0.1 to 100 rad/s while G'' has values about 2 orders smaller than those of G' with a broad minimum part. The dynamic moduli G^*, G', and G'' for the other five samples manifest, though not displayed here, the same features in the ω and γ dependences. These phenomena may suggest that, even if there were considerable charged groups on the network chains, the viscoelastic state of the polyelectrolyte gels would be in the plateau region within the experimental ω range. The relaxation process is too slow to be detected as judged from the order of magnitude of G'' compared with that of G'. In other words, this result seems to suggest that the polyelectrolyte gel would be in the rubberlike state, and the deformation energy acting on it would be completely converted into the elastic energy.

The dynamic storage moduli G' for these six samples were plotted together in Figure 2 as functions of ω. It is found that the plateau level of G' varies with f, the mole fraction of the ionizable monomer AMPS in the network. The equilibrium shear modulus G_e in our case can be considered as equal to the plateau value of G' since the G'' value is negligibly small.[12] The values of G_e evaluated for our six samples are summarized in Table I. All of the G_e values have the same order of magnitude of 10^4 dyn/cm^2, which is less than the usual order of 10^{6-7} dyn/cm^2 for

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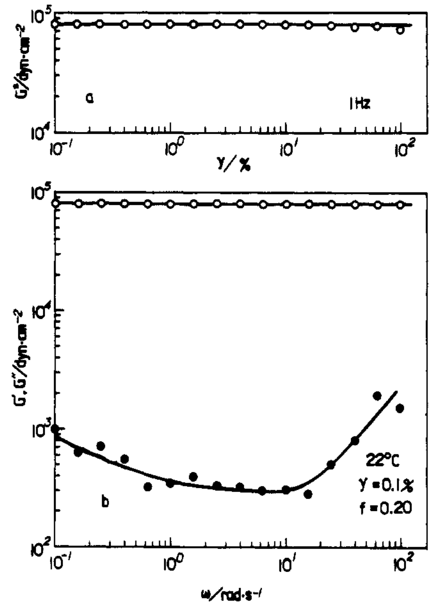

Figure 1. (a) Shear strain γ dependence of the absolute values G^* of the complex modulus and (b) radian frequency ω dependence of storage moduli G' (○) and loss moduli G'' (●) for the sample DS20.

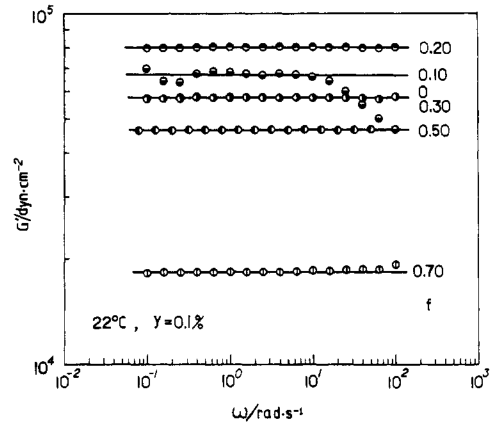

Figure 2. G' vs ω plots for the six gel samples with indicated f values, where the data for the samples of f = 0 and f = 0.30 overlap each other.

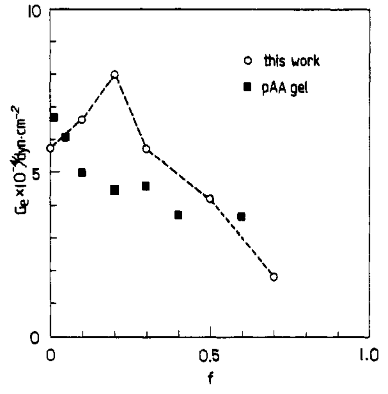

Figure 3. Variation of the equilibrium shear modulus G_e with charge density f for the polyelectrolyte gels: (○) this work; (■) Schosseler et al.[3]

rubbers.[12] Since f values represent the charge density in a given gel sample, the electrostatic interaction contribution to G_e may be revealed more clearly by plotting experimental values of G_e against f as shown in Figure 3. One can find that, with an increase in f, G_e increases and then decreases, reaching its maximum at $f \simeq 0.2$; i.e., the change in the charge density of the samples may alter the equilibrium shear modulus of the polyelectrolyte gels. The uniaxial compression data obtained by Schosseler et al.[3] on partially neutralized poly(acrylic acid) gels of C_t = 1.44 mol/L and C = 0.0047 are also represented in the same figure by the filled squares for comparison. They reported that G_e was monotonically and weakly reduced with an increase in charge density. The f dependence of G_e similar to that of Schosseler et al. has been observed by Takahashi et al. on poly(acrylic acid) gels using the Hertz method.[4] It appears that the influence of f on G_e may be related to the contribution of the electrostatic interaction of charged groups to the elastic energy of polyelectrolyte gels, though the network structure may be affected by the composition of the pregel solutions.

Theoretical Consideration. The HID theory[7] for uniaxial extension is adopted here for a roughly qualitative explanation of the experimental phenomena described above, as we have no other theory available. In this theory, the macromolecular chain is regarded as an assembly of statistical segments carrying charges, the distances between which are governed by the Gaussian distribution, and the electrostatic interaction is calculated by means of the Debye–Hückel theory. Deformation of the gel will cause the conformational change of the network chains, and this change in turn leads to the free energy change.

When the just polymerized gel is chosen as the reference state for simplifying the treatment, G_e is accordingly expressed by

$$G_e = G_{e0}(1 + \phi_N + \phi_E) \tag{1}$$

Here, G_{e0} is the modulus known from the classical theory of rubber elasticity. ϕ_N is the contribution of the limited extensibility of highly swollen chains which will not be discussed here for it has nothing to do with the charge density. ϕ_E is the contribution of the electrostatic interaction which is expressed as follows:

$$\phi_E = i^2\epsilon^2Z^2/DkT[\langle R_0^2\rangle(\lambda^2 + 2/\lambda)^3/3]^{-1/2} \times [A/(1 + A) - \ln(1 + A)] \tag{2}$$

with

$$A = [3DkT(\lambda^2 + 2/\lambda)/(\pi N_A\epsilon^2\langle R_0^2\rangle\alpha C_t)]^{1/2} \tag{3}$$

In the above equations, i and α are the effective and stoichiometric degrees of ionization, respectively; ϵ is the unit charge, Z the polymerization degree of the chain in the network, D the dielectric constant of the medium, k Boltzmann's constant, T the absolute temperature, $\langle R_0^2\rangle$ the mean-square end-to-end distance in the reference state, λ the macroscopic deformation ratio, and N_A Avogadro's number.

For our polyelectrolyte gels with sulfonic acid groups, both i and α are assumed to be equal to f, and Z is estimated from $Z = \rho\phi_2/M_0\nu_e$ and $\langle R_0^2\rangle$ from $\langle R_0^2\rangle = sZb^2$.[7] Here, ρ is the density of dried gel; ϕ_2 and ν_e are the volume fraction of polymer and the chain density in the gel sample, respectively; M_0 is the equivalent molecular weight of the monomer unit varying with the composition of the sample, b the monomer length of $b = 2.55 \times 10^{-8}$ cm,[8] and s the number of monomer units in the statistical segment. The values for gel sample DS30 of $\lambda = 1.001$, $\rho = 1.243$ g/cm^3 (at 25 °C), $\phi_2 = 8.73 \times 10^{-2}$, $\nu_e = 2.34 \times 10^{-6}$ mol/cm^3, and $M_0 = 132.3$ are used in the numerical simulation, where ρ is experimentally evaluated, and ϕ_2, ν_e, and M_0 for the given sample are estimated from the weight fraction of the polymer, the corresponding G_{e0} value using the classical relation for rubber elasticity,[5,6] and the molecular weights of DMAA, AMPS, and BIS according to the gel composition, respectively. Figure 4 depicts the calculated curves

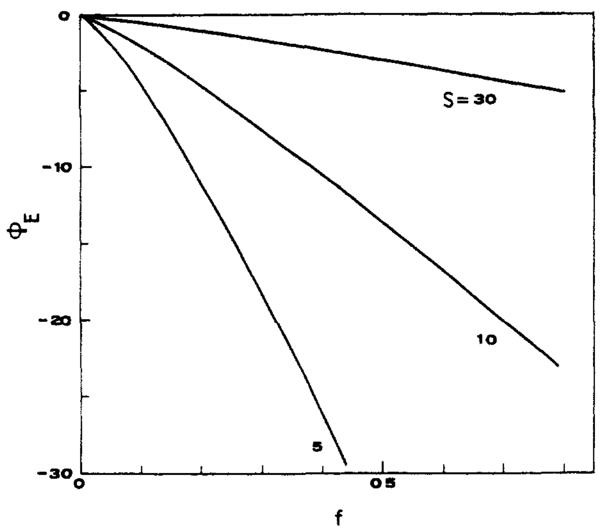

Figure 4. Calculated curves for the f dependence of ϕ_E, the contribution from electrostatic interaction to G_e (see the text for details).

for s values of 5, 10, and 30. It can be found that ϕ_E is always negative and monotonically decreases as f increases. These results seem to say that the existence of charges on the network chains will decrease the equilibrium shear modulus G_e of the polyelectrolyte gels; and the softer the chains (i.e., the smaller the s), the steeper this decreasing effect appears.

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