Influence of solvent quality on the swelling and deswelling and the shear modulus of semi-dilute solution cross-linked poly(vinyl acetate) gels 🔵EP

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ABSTRACT

We systematically examine the influence of varying temperature (T) over a large range in model poly(vinyl acetate) gels swollen in isopropyl alcohol. The theta temperature Θ, at which the second virial coefficient A_2 vanishes, is found to be equal to within numerical uncertainty to the corresponding high molecular mass polymer solution value without cross-links, and we quantify the swelling and deswelling of our model gels relative to their size at $T = \Theta$, as customary for individual flexible polymer chains in solutions. We also quantify the "solvent quality" dependence of the shear modulus G relative to $G(T = \Theta)$ and compare to the gel swelling factor, α. We find that all our network swelling and deswelling data can be reduced to a scaling equation of the same general form as derived from renormalization group theory for flexible linear polymer chains in solutions so that it is not necessary to invoke either the Flory–Huggins mean field theory or the Flory–Rehner hypothesis that the elastic and mixing contributions to the free energy of network swelling are separable to describe our data. We also find that changes of G relative to $G(T = \Theta)$ are directly related to α. At the same time, we find that classical rubber elasticity theory describes many aspects of these semi-dilute solution cross-linked networks, regardless of the solvent quality, although the prefactor clearly reflects the existence of network defects whose concentration depends on the initial polymer concentration of the polymer solution from which the networks were synthesized.

Published by AIP Publishing. https://doi.org/10.1063/5.0156604

I. INTRODUCTION

Polymer networks constitute an enormous and growing class of materials ranging from plastics, hydrogels having both chemical and associative bonding and porous frameworks used for catalysis, and molecular separation.[1] Hydrogels formed in water or other hydrogen bonding solvents have recently been of particular interest in connection with their use in diverse emerging regenerative medicine, tissue engineering,[2,3] and drug delivery[4] applications. There are also many new types of synthetic gels developed in materials science applications related to manufacturing where the chemistry has been tailored to meet particular end uses.[5] A wide range of material

properties have already been achieved in many natural materials formed in this way through the selective pressures of evolution. There is also great interest in marine hydrogels in relation to carbon sequestration in the oceans and climate change[6] and in understanding the turgor in plants and controlling the juiciness and hardness and other aesthetically important properties of foods.[7]

Since essentially any form of condensed matter, even crystalline materials, can be formally described as a polymer network if the bonding is allowed to involve both chemical and associative bonds, we cannot expect a single theoretical framework to describe the swelling and elasticity of this broad class of materials when temperature or other thermodynamic variables are altered. Early work

aimed at understanding the thermodynamics and mechanical properties of rubbers in which there was little or no solvent emphasized entropic changes of the flexible polymer chains comprising these materials. Modeling this class of materials, where the "dry rubber" was naturally chosen as the reference state, gave rise to the now classical theories of rubber elasticity developed by James and Guth[8] and Wall and Flory,[9] and the simple model of Flory and Rehner[10,11] allowed for the description of the swelling of these materials by combining the classical rubber elasticity model with the mean field Flory–Huggins theory of the free energy of mixing polymers with solvents. In particular, the Flory–Rehner model does not distinguish between stretching arising from deformation and swelling, and this type of model treats the elastic contribution to the free energy to be completely separable from the "mixing" contribution arising from interchain interactions that cause both flexible linear and network chains to swell or contract depending on temperature or other thermodynamic variables that alter the intermolecular excluded volume interaction or "solvent quality." Although this theoretical framework is often applied to rather different types of networks, such as hydrogels or polymers cross-linked in semi-dilute solution, this generalization is known to be problematic because fluctuation effects prevalent in polymer solutions can give rise to large deviations from this type of mean field theory.

A "scaling theory" of polymer solutions addressing these fluctuation effects was developed by de Gennes,[12,13] first for linear polymer chains in dilute and semi-dilute polymer solutions, and this type of argument was later applied with success by others to swollen polymer networks formed by cross-linking of long polymer chains in solutions, where it was found that the networks preserved the scaling properties of the osmotic pressure of polymer solutions to an excellent approximation. It is notable here that the thermodynamic properties deduced by the scaling theory are *not consistent* with the Flory–Huggins theory,[14,15] which is particularly important when it comes to modeling the effects of variable excluded volume interactions on polymer swelling and "syneresis" in which the solvent is ejected from the network as a kind of intramolecular phase separation process. The scaling theory applies mainly to the good solvent limit, although scaling arguments have also been developed for polymer solutions under "theta solvent" conditions where the second virial coefficient of long polymer chains in solution vanishes so that the chain dimensions can be reasonably idealized as being Gaussian to a good approximation, at least in the case of linear polymer chains.

The treatment of the swelling and shear rigidity of polymer networks formed by chemical cross-linking of flexible chains in solutions as a function of variable solvent quality requires a more general framework that must include some sort of "hybridization" of ideas drawn from the Flory–Huggins and scaling theories to describe how changing polymer solvent quality alters the dimensions and elastic properties of the particular class of network, which subsumes many hydrogel materials and many "gel" materials of interest in manufacturing. We mention here that while the problem of network swelling becomes theoretically more complicated in some ways than the situation of linear polymers, the preparation of the networks in semi-dilute solutions can also bring significant simplifications because the interchain interactions responsible for chain entanglements can be *strongly suppressed* in these systems. Somewhat ironically, this situation leads to much better agreement between the elastic

properties of "gel" networks and the classical rubber elasticity theory than in the case of dry rubber materials where the interchain interaction effects are clearly prevalent, especially at low network cross-linking densities where these interactions dominate the network elasticity.

Our task of studying swelling in gels is also made easier by the accumulation of a large amount of high precision and laboriously acquired experimental data on solvent quality and shear moduli observations on this type of network over the last 50 years. These data can serve to check any theoretical framework proposed to describe thermodynamic and static and dynamic scattering properties of these materials. In this initial study, we confine our attention to the changes in network chain dimensions and shear modulus when the solvent quality is varied from very good, corresponding to temperatures far above the theta point, to very poor where the solvent is ejected from the gel, ultimately forming a "dry" gel when all the solvent has been removed in this way. While polystyrene in various organic solvents has found favor as the go-to model in experimental studies of swelling and chain conformation of flexible linear polymers in solutions, poly(vinyl acetate) (PVAc) with glutaraldehyde as a cross-linking agent has this distinction as a model polymer of choice in numerous studies of gel networks formed in semi-dilute solutions.[16–20]

We utilize this established database as the foundation of the present study aimed at describing solvent quality effects on the swelling and elastic properties of this class of polymer gels. We should mention that there have been many recent studies of the swelling of polymer networks[21–24] based on classical rubber elasticity theory and Flory–Huggins theory-type modeling. Our treatment is based on a different theoretical framework that tries to avoid the assumptions of previous modeling as much as possible, but our efforts still owe a great debt to previous theoretical modeling efforts and computational studies mentioned below that provided some guidance about how to organize and analyze our PVAc gel data.

II. THEORETICAL CONSIDERATIONS

As a starting point, we note that rather extensive progress has been achieved based on the renormalization group (RG) theory in describing the swelling and osmotic properties of flexible linear polymers under variable solvent quality conditions and there has been a large body of work validating this theory. It is then possible to avoid treating swelling of linear polymers in semi-dilute and dilute polymer concentrations by the inadequate Flory–Huggins theory, and crossover results for polymer solution properties may be formally derived under variable solvent quality conditions. A similar reduced variable description is our target for gels.

Correspondingly, there have also been RG calculations for randomly cross-linked networks, although this theory has not been subjected to tests as in the case of linear polymers. Recently, Chremos *et al.*[25] studied model branched polymer networks with variable excluded volume interaction where it was found that the swelling and theta point exponents of randomly branched polymers agreed within experimental consistency with theoretically predicted values and they were able to describe the dimensions of networks containing chains of different masses at all temperatures simulated,

corresponding to very poor, theta, and good solvents by the same crossover expression deduced from the leading order expansion theory for linear polymer chains. This raises the possibility that we might be able to reduce our PVAc gel data over a wide range of solvent quality by the same RG scaling form. We show below that this is the case, but first, we must discuss an unexpected technical issue that is related to the conditions of chemical cross-linking that can greatly influence the swelling and mechanical properties of polymer networks.

The PVAc networks are synthesized by cross-linking of relatively long polymer chains in solutions (see Sec. III) under conditions in which linear precursor chains are swollen so that standard scaling theory describes the osmotic and elastic properties of these materials both before and *after* cross-linking. This corresponds to a swelling exponent v near the well-known Flory estimate of $v \approx 3/5$, and the concentration scaling exponent for the shear modulus of the cross-linked material scales with a power close to 2.25. The observations by Geissler *et al.*[26] on polyacryl amide gels provide a good example of this type of scaling, which is also expected for the present PVAc gels.

This good solvent scaling behavior has recently been observed for some gels made in a similar fashion.[27] However, while the exponent estimate corresponding to $v \approx 3/5$ makes sense for linear chains, it has been rigorously established that the swelling exponent v for an equilibrium ensemble of randomly branched polymers or "network polymers" is *exactly* $v = 1/2$ in three spatial dimensions.[28] From this result, we would expect the well-known scaling relation that the osmotic pressure and shear modulus should scale with the polymer volume fraction as φ^3. This alternative scaling is clearly observed in simulations of Chremos *et al.*[25] for their swollen network polymers, and it has also been observed experimentally in the scaling of the osmotic modulus and the corresponding scaling of the correlation length ξ with polymer concentration $\xi \sim \varphi^{-1}$ in *swollen N*-propyl acrylamide (NIPAM) gels under good solvent conditions.[29] Recent simulation work[30] has further confirmed this scaling. To reconcile our present measurements with the expected scaling of swollen random networks, we hypothesize that cross-linking high molecular mass polymers in semi-dilute solutions "lock in" the network into a *non-equilibrium state* that cannot relax their configurations due to topological restrictions fixed by cross-linking. This definitely creates a problem for our analysis, but since this type of "memory effect" is probably generic in cross-linked and knotted polymers (see Sec. IV), we proceed in our effort in organizing the network swelling and modulus data based on the tentative assumption that $v \approx 3/5$ in the present PVAc networks under good solvent conditions, in consistency with the "parent" polymer solution from which the polymer network was fabricated.

III. MATERIALS AND METHODS

A. Preparation of polyvinyl alcohol gels

Polyvinyl alcohol (PVA) solutions of different concentrations (c = 3.0, 6.0, 9.0, and 12.0 mass%) were made in water and cross-linked with glutaraldehyde (GDA, Merck) at pH = 1.5 at 25 °C.[16,31,32] A fully hydrolyzed and fractionized PVA sample (M_m = 110 kDa) was used. The average chain length between neighboring cross-links was varied from 50 to 400 monomer units. Cylindrical gel specimens (1 cm in diameter and 1 cm in height) were made from the

mixture of a polymer, cross-linker, and catalyst (2 N HCl solution) in a mold. After gelation, the gel samples were equilibrated with distilled water to remove HCl and unreacted polymeric materials. Then, gels were swollen in water/*n*-propyl alcohol mixtures containing gradually increasing amount of *n*-propyl alcohol.

B. Preparation of poly(vinyl acetate) gels

Poly(vinyl acetate) (PVAc) gels were prepared from PVA gels.[18,31,32] PVA gels swollen in water were placed in a mixture of acetic anhydride (40 vol. %), acetic acid (10 vol. %), and pyridine (50 vol. %). The acetylation reaction was carried out at 90 °C for 8 h. The acetylation mixture was renewed hourly. In the last 3 h, the acetic acid was omitted from the mixture in order to shift the equilibrium to the direction of acetate formation. The gel samples were washed with toluene. This process involved at least ten solvent exchanges and took over several weeks. Then, the PVAc gels were dried. The extent of acetylation was measured, and an agreement within 1% to 2% was found between the calculated and experimentally determined values. The dry networks were swollen in isopropyl alcohol. The gels were kept 1 month at each T before testing.

C. Shear modulus measurements

The shear modulus of the gels was determined using a TA.XT2I HR texture analyzer (Stable Micro Systems, UK), which measures the deformation as a function of the applied force.[33] Uniaxial compression measurements were performed on cylindrical gel specimens equilibrated with the appropriate swelling agent. Typical sample sizes were 0.5–1 cm in height and 0.5–1 cm in diameter. The shear modulus G was calculated from the nominal stress, σ (force per unit undeformed cross section), using the phenomenological Mooney–Rivlin relation,[34]

$$\sigma = 2(\lambda - \lambda^{-2})(C_1 + C_2/\lambda), \quad (1)$$

where λ (=L/L_o, L and L_o are the lengths of the deformed and undeformed gel specimen, respectively) is the deformation ratio and $C_1 + C_2$ are constants. Uniaxial compression measurements were made in the range $0.7 < \lambda < 1$ (note that in compression, σ is negative).

In Fig. 1, typical reduced stress $-\sigma/(\lambda - \lambda^{-2})$ data vs λ^{-1} are shown for PVAc and PVA gels swollen in good, theta, and poor solvents. It is apparent that the value of C_2 is approximately zero in both systems, so in the sense of conforming to classical rubber elasticity, these polymer gels formed by cross-linking polymers in solutions are "ideal." Many previous observations on solution cross-linked gels are consistent with our observations, and this scaling behavior can be taken as being characteristic of this class of gels. Correspondingly, $2 C_1$ can be identified with the shear modulus G of our gels. Evidently, G is smaller in a good solvent and increases as the solvent quality decreases.

The duration of a stress–strain test was varied between 5 and 10 min. The absence of volume change and barrel distortion during these measurements was carefully checked. Mechanical tests were performed at 25 °C (PVA/water, *n*-propyl alcohol gels) and at 30, 37, 45, 50, 52, 55, 60, and 70 °C (PVAc/isopropyl alcohol gels). The reproducibility of the whole procedure, including gel preparation, and G measurements was found to be within 4% to 5%.
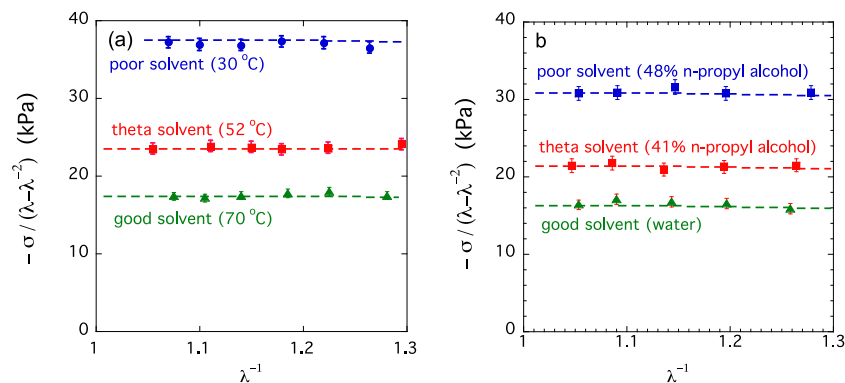
FIG. 1. Typical $-\sigma/(\lambda - \lambda^{-2})$ vs λ^{-1} plots for PVAc and PVA gels in good, theta, and poor solvents. (a) PVAc/isopropyl alcohol gels at (30, 52, and 70 °C). (b) PVA gels swollen in pure water and 41% *n*-propyl alcohol and 59% water and 48% *n*-propyl alcohol and 52% water mixtures.

IV. RESULTS AND DISCUSSION

As noted above, polyvinyl alcohol (PVA) and its acetylated derivative polyvinyl acetate (PVAc) have served as a model gel material for many years and a large body of high-quality measurements on these materials has now accumulated. Of particular interest for the present work is a series of measurements on the mechanical and swelling properties of these polymers by Horkay and Zrinyi.[16,31,32] This work was later extended to numerous comprehensive static neutron and light scattering studies aimed at interrelating the macroscopic osmotic measurements to scattering intensity measurements and to separate thermodynamic from static contributions to the scattering response and to determine the concentration correlation lengths of these materials.[35,36] Polyacrylamide gels served as a model system for now classical dynamic light scattering studies by Tanaka and co-workers[37–40] relating to quantifying collective diffusion in these materials. Systematic studies were made to determine the osmotic compressibility, the interrelation between the static and dynamic correlation lengths from static and dynamic light scattering measurements,[41] the rate of gel swelling,[42–44] gel permeability,[45–49] non-ergodic dynamics of the gel state,[50] interfacial instabilities in gels,[51] and local fluctuations in shear modulus fluctuations based on atomic force microscopy.[52] The mechanical and swelling properties of composite gels consisting of a PVA gel matrix with polyacrylic acid microparticles dispersed in it were found to mimic the swelling pressure of human cartilage.[53] There has also been a large body of measurements performed with the aim of understanding fundamental aspects of the swelling–deswelling transition,[54–56] phase separation in gels,[56–60] and the observation of negative values of the Poisson ratio near the swelling–deswelling or "collapse" transition.[61,62] This accumulated body of data serves as a valuable resource for researchers seeking to develop a better understanding of gels. We next draw specifically upon accumulated data[31,32] for the swelling and mechanical properties of PVAc gels over an exceptionally wide range of T to explore the impact of solvent quality variation on these properties with the aim of obtaining a universal reduced variable description of network swelling that can be used in many applications of gel materials, including medical science and manufacturing.
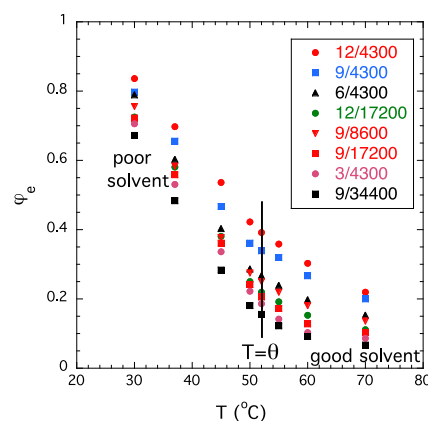

FIG. 2. Equilibrium swelling concentration φ_e for PVAc gels in isopropyl alcohol synthesized at various initial polymer concentrations and for a range of the average chain molecular mass M_{net} between cross-links. M_{net} was calculated based on the stoichiometry of the cross-linking process.

A. Influence of solvent quality on PVAc network swelling

In Fig. 2, the equilibrium swelling concentration φ_e of PVAc gels as a function of temperature is shown. The initial polymer concentration ranges from 3% to 12% polymer mass percent, and the temperature range varies between 30 and 70 °C. The cross-linking density is sufficiently high that all materials are in the "gel" state for which the equilibrium shear modulus (discussed below) is finite. We quantify the cross-linking density by the average mass between cross-links and the average mass of the network chains M_{net}, which we estimate from the stoichiometry of the cross-linking process. For example, if the ratio of the number of monomer units to the number of cross-linker molecules is 100, then $M_{net} = 100 \times 86 = 8600$ (86 g/mol is the molecular mass of the vinyl-acetate monomer). In Fig. 2, we designate different gels by a numerical pair in which the left number is the mass percent of the polymer at cross-linking and the number on the right is M_{net}.

Next, we seek to introduce an appropriate reduced variable description of our swelling data based on what is collectively known theoretically about network swelling and drawing upon previous simulation and experimental studies of excluded volume effects on the swelling and mechanical properties of gels. First, it is generally known that the theta point at which binary excluded volume interactions of long flexible polymers vanish corresponds to a natural reference temperature of polymer solutions. The "theta temperature" Θ is 52 °C for PVAc homopolymer in isopropyl alcohol, and we take that this reference temperature also describes the theta condition for our gel material, with an understanding that the glutaraldehyde cross-linking agent and the physical constraint of the cross-links might slightly alter this characteristic temperature.

We may assess the assumption of the near invariance of the theta temperature to cross-linking in PVAc gels swollen in isopropyl alcohol through a direct measurement of the second virial coefficient A_2 as a function of T. We also check this possibility independently below in connection with the concentration scaling of the shear modulus data. The theta temperature Θ is analogous to the Boyle point in non-ideal gases and corresponds to the temperature at which attractive binary excluded volume interactions compensate repulsive binary excluded volume interactions so that the excluded volume effect on the osmotic pressure vanishes to leading order in the concentration, i.e., $A_2 = 0$. We have previously determined A_2 as a function of T for PVAc gels in isopropyl alcohol,[63] and we show its variation with T in the inset of Fig. 3(a). Consistent with our hypothesis that there is only a little change with cross-linking, we see that the theta temperature Θ of the cross-linked gel is indeed close to the theta temperature of the corresponding polymer solution. We also indicate the third osmotic virial coefficient A_3 of the PVAc gels in isopropyl alcohol, which is normally reported as a concentration dependent contribution to the Flory–Huggins χ-parameter.[63] A_3 is expected to be relatively insensitive to a variation of T, but to vary appreciably with the cross-linking density.[64] We plan to investigate this important phenomenon in a separate publication. Regarding this important issue, we refer the reader to the inset of Fig. 2 of Ref. 65 where the concentration independent (χ_0) and concentration dependent (χ_1) contributions of the Flory χ-parameter for a range of cross-linking densities are indicated. This is basically just an equivalent of a different notation for the second and third virial coefficients, which can be directly expressed in terms of χ_0 and χ_1; see Eq. (3) of Ref. 63 for the exact correspondence between these χ_i parameters and the osmotic virials (A_2, A_3). After making this simple transformation, we see that A_2 is nearly invariant to cross-linking, while the magnitude of A_3 is appreciably altered in magnitude for these relatively well-characterized model tetrapoly(ethylene glycol) hydrogels. Horta and Pastoriza[66] have recently reviewed the extensive literature on the cross-link dependence of the concentration dependent Flory–Huggins χ-parameter in polymer networks and branched polymer solutions.

Following standard practice for dilute polymer solutions, we defined a reduced temperature, $\tau = (T - \Theta)/T$, as a basic measure of "solvent quality," where $\tau < 0$ corresponds to a "poor solvent" and $\tau \gg 0$ corresponds to a "good solvent." In Fig. 3(a), we show the gel "swelling factor" α^3 (gel volume relative to its volume at Θ) as a function of the reduced temperature, τ. The swelling curves cross at $\tau = 0$, again similar to the swelling of homopolymer chains in solutions where the rate of swelling or contraction of the chains is

likewise more rapid when the mass of the chains is larger[67,68] In a recent study of the swelling of polymer networks through varying solvent quality and M_{net} by Chremos et al.,[25] a very similar pattern of swelling was found, and we closely follow this work in our analysis below. Note that this philosophy of reducing our data in relation to a theta point rather than the dry rubber material reference state is in accord with a view strongly advocated previously by Khokhlov.[69]

The next requirement in the development of a reduced variable description of the swelling and deswelling of polymer networks is the definition of an excluded volume interaction parameter appropriate for cross-linked materials that addresses the dependence of the excluded volume interaction on the mass of the network chains. To define this reduced excluded volume interaction, we follow the approach of Zrinyi and Horkay,[31,32] which is based on a combination of the James and Guth theory[8] and a formal virial expansion approximation of the free energy contribution related to the mixing free energy, including contributions up to the third virial coefficient. Notably, this argument does not assume that the Flory–Huggins mean field model applies, but a separability between the elastic and mixing free energies is assumed in the theoretical argument of Zrinyi and Horkay.[31,32] This argument leads to the conclusion that the natural excluded volume parameter for gel networks corresponds to τ/φ_θ, where $1/\varphi_\theta$ is defined as the ratio of the volume of the gel under theta conditions to its value in its dry state $V_{gel,dry}$,

$$1/\varphi_\theta \equiv V_{gel,\theta}/V_{gel,\,dry}. \tag{2a}$$

We may then define our dimensionless excluded volume interaction variable z_g by the relation,

$$z_g = (\tau/\delta\,\varphi\theta), \tag{2b}$$

where the constant δ is uniquely fixed by demanding that the leading order expansion expression for α^3 is given by,

$$\alpha^3 \equiv 1 + z_g + O(z_g{}^2), \tag{3}$$

for *all* cross-linked gels. It is emphasized that the constant δ is non-universal, i.e., it varies with solvent and polymer type as in the analogous case of flexible polymers in solutions.[67] We view the parameter δ as being analogous to the viscosity parameter η in the Navier–Stokes equation, which is a material specific parameter that absorbs a host of many body-effects associated with intermolecular interactions that are beyond the scope of this coarse-grained general model of the dynamics of liquids in the limit of low Reynolds number. It is important to realize that this definition of the dimensionless excluded volume interaction for gels cross-linked in solutions subsumes the influence of three-body interactions that can be important in gels because of the higher probability of this type of interaction in branched polymers.[70,71] Such interaction also becomes appreciable when attractive polymer–polymer interactions become significant.[27,72]

Zhulina et al.[73] gave a more sophisticated discussion of the appropriate choice of the dimensionless excluded volume interaction in the context of the problem of the swelling and deswelling of polymer-grafted layers based on density functional methods, where they found the *same* excluded volume interaction variable as in Eq. (2). This correspondence is natural since Karim et al.[74] argued that one can think of densely grafted polymer brushes as being a
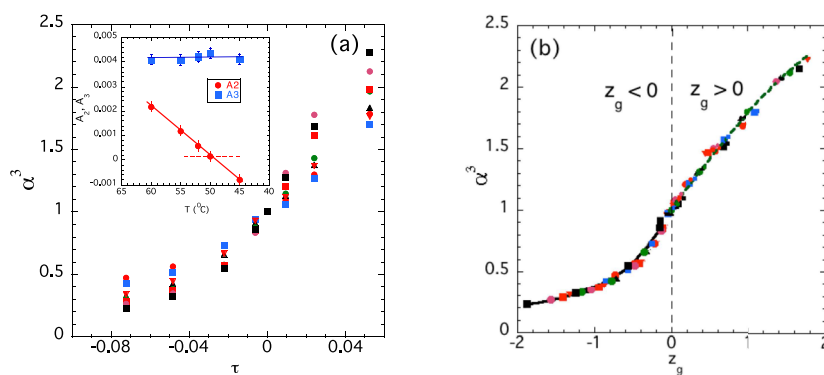
FIG. 3. Swelling and deswelling of solution grafted polymer networks. (a) Volumetric swelling factor α^3 for PVAc-isopropyl alcohol gels vs reduced temperature τ. The inset in (a) shows the variation of the second and third virial coefficients as a function of T. (b) α^3 vs excluded volume interaction parameter z_g ($\equiv \tau/\delta \, \varphi_\theta$) for PVAc-isopropyl alcohol gels. The continuous line is the fit in the deswelling regime below Θ ($z_g < 0$). The dashed line is the fit in the good solvent regime ($z_g > 0$). In (b), the maximum deviation from the least squares fit is less than 3%.

particular type of polymer network in which all the "cross-links" are confined to a boundary and Karim *et al.* verified this perspective by showing that the swelling and deswelling of polymer brushes and solution cross-linked polymer gels could be well-described by this dimensionless variable over a wide range of excluded volume interactions. The gel data used in this study correspond to PVAc gels swollen in isopropyl alcohol, the same material considered in the present work.

We show in Fig. 3(b) that all our swelling and deswelling data of PVAc gels can be described by this reduced variable description to a good approximation for all initial polymer concentrations φ_o and average network molecular mass M_{net} (cross-linking densities) values and for the entire range of T investigated in previous works. Note the linear variation of α^3 in z_g around the theta point where $z_g = 0$ extending over the range [−0.5, 0,5], in consistency with Eq. (3) when z_g is small. The dimensionless gel swelling curve appears to be remarkably "universal," at least for this particular type of polymer (see Sec. IV), and again, we observe a close superficial similarity with swelling data often observed for the radius of gyration (R_g) of flexible polymer chains in solution[67,68,75] when T is varied over a broad range.

We may further quantify the specific functional form of $\alpha(z_g)$ based on a recent study[27] of the swelling of polymer networks as a function of variable excluded volume interaction, where it was found that existing RG predictions for the effect of polymer excluded volume interactions in linear and randomly branched polymers can be combined to make a prediction for $\alpha(z_g)$ suitable for network polymers in which z_g is positive. (Unfortunately, the RG method is not applicable in the regime where z_g is negative[76,77] and the polymer chains become unstable and collapse to form a compact globular structure, but we address the limit below based on a previous scaling argument of Zrinyi and Horkay.[31,32]) In particular, Chremos *et al.*[25] found that the perturbation theory RG expression of $\alpha^2(z_g)$ well describes their model polymer network swelling data for all T and M_{net} simulated, although the swelling exponents in good and theta solvents were changed to values appropriate to randomly branched polymers. In our PVAc gels cross-linked in semi-dilute solutions

rather than generated as an equilibrium network, we expect the swelling exponents to preserve the geometry of the linear chain precursors from which the network was constructed.

We next compare our gel $\alpha(z_g)$ data in Fig. 3(b) to the same RG theoretical expression as considered before by Chremos *et al.*,[25] but with the exponents taken to equal those of self-avoiding linear polymers rather than randomly branched polymer chains where the measured excluded volume interaction variable z_g is taken to be proportional to the excluded volume interaction parameter z_2 of the RG theory,[78]

$$\alpha^2(z) = \left(1 + z_2/u^*\right)^{(2\nu-1)/\varphi}\left[1 + b(z_2/u^*)/(1 + z_2/u^*)\right], \; z_2 > 0. \tag{4}$$

In Eq. (4), $(2\nu − 1)/\varphi$ equals 2/5 using the Flory approximation of $\nu \approx 3/5$ for swollen linear polymers in $d = 3$ and the constant b is taken to be empirical. In the case of flexible linear polymers, the parameter b is precisely determined from a renormalization group (RG)-based resummation of the "two-parameter theory" perturbative expansion[67] or "Fixman expansion" in the dimensionless excluded volume interaction variable z of polymer configurational properties that provide average measures of polymer size, such as the mean square radius of gyration R_g^2, the polymer end-to-end distance $\langle R^2 \rangle$, and intrinsic viscosity [η]. The implementation of the RG methodology requires that the two parameter theory expansions be performed in d spatial dimensions because this method also involves a perturbative expansion in the dimensional parameter, $\varepsilon = 4 − d$.[68] Standard two-parameter theory calculations, as found by Yamakawa,[67] are normally restricted to three dimensions $d = 3$, but these calculations still provide sufficient information for estimating b for many polymer solution property calculations performed earlier using the standard two parameter theory.[68] It is emphasized that b is a *property specific* constant that is also dependent on molecular topology (ring, star, comb, etc.). However, its magnitude usually does not vary much between properties, providing a similar measure of polymer "size," even if the polymer topology is varied.[68] This situation explains why we treat b as an empirical constant.

In the RG theory, u^* is a characteristic constant that roughly describes the interaction range over which the linear approximation in Eq. (3) applies. For the purposes of the present work, the RG constant u^* can be absorbed into the dimensionless excluded volume variable, z_g. In particular, by assuming that z_2 of Eq. (4) is proportional to z_g and then expanding Eq. (4) and matching this expansion to the expansion in Eq. (3), we may uniquely fix the constant relating z_2 to the experimentally determined z_g. The fit of Eq. (4) to our data in Fig. 3(b) yields the precise relationship, $z_g = 1.61 z_2$.

In general, Eq. (4) is predicted to apply for any linear measure of polymer size (e.g., radius of gyration) and to any polymer topology within the linear polymer universality class (linear, ring, comb, star polymers, etc.) where the constant b is polymer and molecular topology specific.[68,79,80] Douglas et al.[81] gave a general expression for $(2\nu - 1)/\varphi$ for linear self-avoiding polymers, which is exact in one, two, and near four dimensions and which yields a precise numerical estimate in $d = 3$ that is consistent with the best numerical estimates. We again note that the RG expression for $\alpha^2(z_g)$ in the case of linear polymers is just the result of resuming terms through all orders in z in the familiar two-parameter perturbation theory of polymers.[67,68] Interestingly, the large z_g asymptotic scaling of $\alpha(z_g)$ predicted in Eq. (4) coincides with the scaling arguments given by Zrinyi and Horkay[32] for the large repulsive excluded volume interaction regime where $\alpha(z_g) \sim z_g^{1/5}$ for $z_g \to \infty$.

Although there is no RG treatment of self-attracting polymers, scaling arguments offer some guidance on what to expect in this regime. In this case, the predictions seem to be useful, even though the existence of universality is more questionable in the regime of polymer deswelling because of the role of many-body interactions.[72] As noted before, we may hope that the definition of z_g, which accounts for ternary interactions, is sufficient in the self-attracting polymer regime when the strength of these interactions is large, but this remains to be shown through an examination of measurements on many well-characterized gel systems. The solid line in Fig. 3(b) in the negative z_g regime shows that the simple scaling theory prediction,[82] $\alpha^3 \sim 1/|z_g|$, describes all our data to a remarkable degree

of approximation, where we estimate the proportionality constant to equal 0.34. This scaling relation needs to be checked in other systems before it can be accepted as being "universal" in the deswelling regime, but the results of Fig. 3(b) are encouraging regarding the applicability of the scaling theory to this regime. We note that Nierlich et al.[82] observed R_g of polymer chains in solutions in the collapsed regime R_g (collapse) scale approximately as $R_g \sim |\tau|^{-1/3}$, consistent with the T dependence of the gel dimensions implied by the $\alpha^3 \sim 1/|z_g|$ scaling in Fig. 3(b) for macroscopic gels formed by crosslinking semi-dilute polymer solutions, confirming de Gennes scaling theory[83] for polymer solutions, so this scaling behavior is possibly general. We emphasize that while the apparent scaling exponents for strongly attractive and repulsive interactions seem to be consistent with the theory, over the limited range of z_g for which we have observations, the inherent scattering of the data make the precise estimate of asymptotic scaling exponents in either regime uncertain. The precise estimation of these exponents will have to await future study.

Erman and Flory[84] investigated the influence of ternary interactions in the self-attraction regime based on a self-consistent mean field theory, and they concluded that the smooth variation of α with T seen in Fig. 3(b) can change to a near discontinuous change in the network dimensions as T is varied when ternary interactions are sufficiently large. Dusek also stressed the importance of these higher body interaction effects on network deswelling.[58] This type of sharp change of dimensions is known to be prevalent in polyelectrolyte gels where the ternary interactions tend to be quite large and sensitive to higher valent salts.[63,85] We discuss the conditions in which this "volume phase transition" occurs in Sec. IV.

The dependence of the excluded volume interaction on the mass of the network chains M_{net}, the polymer concentration at which the network was synthesized, and other molecular information related to sample preparation and molecular geometry are "buried" in quantity $1/\varphi_\theta$ in Eq. (2). To get at this information, we directly consider how $1/\varphi_\theta$ depends on M_{net} in Fig. 4. The inset in Fig. 4 indicates that $1/\varphi_\theta$ scales as $1/\varphi_\theta \sim M_{net}^{0.37}$. This apparent scaling exponent differs from the exponent of $1/2$ suggested for the dimensionless excluded volume interaction by Khokhlov,[69] but this value seems to be reasonably consistent with the estimate of $3/8$ obtained by Obukhov et al.[86] for the scaling of the inverse network density at the theta point with M_{net}. Arguments by Grosberg and Nechaev[87] attribute non-trivial ternary interactions in polymer networks to topological constraints that influence the probability of polymer–polymer contacts, which might be relevant to this unexpected scaling, and this possibility deserves further study. Again, the data are too limited to assign a precise measure of the uncertainty of this exponent.
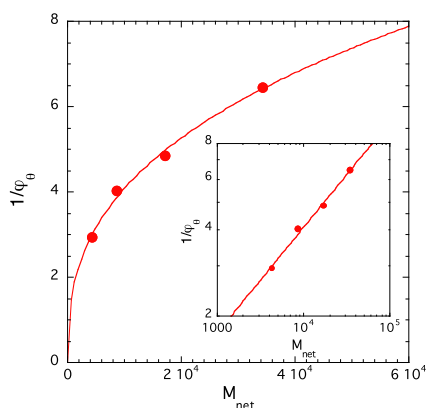

FIG. 4. Theta swelling factor $1/\varphi_\theta$ as a function of average network chain mass M_{net} for PVAc gels prepared at 9% (m/m) polymer concentration swollen in isopropyl alcohol under theta conditions (at 52 °C). The inset shows a plot of log($1/\varphi_\theta$) vs log M_{net}.

B. Influence of solvent quality on the elastic modulus of PVAc gels

We now extend our consideration to how the shear modulus becomes altered under conditions of variable excluded volume interactions, where there is less available theory to guide our analysis. First, we consider the reduced shear modulus G/RT data taken from the work of Zrinyi and Horkay[30,31] in Fig. 5 for PVAc gels swollen
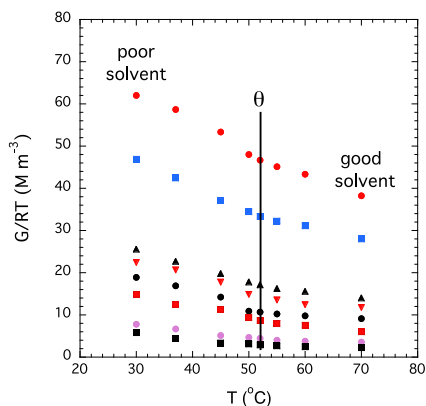
FIG. 5. Reduced shear modulus G/RT vs temperature of PVAc gels swollen in isopropyl alcohol. The gels were made at various initial polymer concentrations with different cross-linking densities. Symbols are the same as in Fig. 2.

in isopropyl alcohol for a range of initial polymer cross-linking concentrations φ_o, variable M_{net}, and the same range of T as considered in our discussion above for $\alpha(z_g)$. We can see the unsurprising trend that these gels become stiffer when the initial polymer concentration and cross-link density are higher.

We test our attribution of the theta point of the gel to that of the corresponding polymer solution, at least to a reasonable approximation, by examining the dependence of G/RT on the equilibrium concentration of the swollen gel shown in Fig. 6. We can see that G/RT scales with a power of φ_e that depends on the temperature. At high temperatures, the apparent exponent n, estimated from the scaling theory, is given as $n = 3\nu/(3\nu - 1)$. The observed experimental value of n is consistent within experimental uncertainty with the predicted good solvent value 2.25, corresponding to the self-avoiding linear polymer value (Flory estimate of $\nu \approx 3/5$), and at the theta temperature of the high molecular mass polymer solution, we observe that the scaling exponent is near the predicted value $n = 3$. As noted above, measurements have consistently shown that the shear and osmotic moduli of solution cross-linked gels scale similarly as a function of polymer concentration.

Figure 6(b) shows similar data for PVA gels swollen in water/n-propyl alcohol mixtures. In this system, the theta composition is 59% water and 41% n-propyl alcohol. Tuning the solvent composition causes a variation of the exponent of the elastic modulus vs polymer concentration plots, although this means of varying the solvent quality often brings with it complications associated with differential partition of the solvent components to the interfacial region of the polymer.

We also note that G/RT extrapolates to a common maximum value corresponding to the material in its dried state, $\varphi = 1$, which is something that we had not initially anticipated. Apparently, neither the variation of the initial polymer concentration under the conditions of cross-linking nor the mass of the network chains alters this limit. This does not mean that the polymer occupies the entire space of the material, but rather, this limiting condition refers to a maximum concentration of the "dried" polymer material at a given T (taken to the be room temperature in the present work). As in the packing of hard spheres, the actual volume fraction occupied can be

considerably less than 1. The "volume fraction" φ thus represents a relative volume fraction in comparison to the material in its dry state.

The same data as in Fig. 6 are viewed from another angle in Fig. 7, where we emphasize trends arising when T is varied for networks of fixed values of initial cross-linking density and initial polymer concentration. The log–log plot indicates that G/RT scales as $\varphi_e^{1/3}$ as one would expect from the classical rubber elasticity theory of James and Guth[8] and the off-sets in the curves in Fig. 7 provide evidence that G/RT depends on the initial polymer concentration. We again show similar results for PVA gels in water and n-propyl alcohol/water mixtures.

It is apparent from Fig. 7(b) that the elastic modulus G non-linearly depends on the initial polymer concentration φ_o before cross-linking. This is expected because of the highly defective nature of the cross-linked network containing both dangling ends and closed rings.[88,89] There has recently been an intense study on these defects in the form of both dangling ends and closed rings[90–92] and the influence of such defects on the elasticity of polymer networks cross-linked in solutions.[90–96] Quantitatively resolving the relative fraction of various types of defects and their contribution to the number of effective network chains to the network topology dependent prefactor of G remains a problem, even though the works just cited give many insights into this difficult problem. *A priori* predicting the number of defects under a given set of synthesis conditions and the ultimate elastic properties of the solution cross-linked gel material is an even greater challenge.

One of the important findings of recent studies of defects in polymer networks formed by cross-linking polymer solutions is the common finding that the fraction of network defects in certain model networks[91] that allow for the quantitative study of network defects depends on the polymer concentration (polymer mass concentration, c) relative to the polymer overlap concentration c^* so that we may generally expect the number of network defects to decrease progressively by increasing the initial polymer concentration, φ_o. (Below, we discuss more recent attempts to model the concentration dependence of defects and network elasticity based on the seminal work of Ref. 91.) The observed trend in Fig. 7(b) is qualitatively consistent with this expectation, i.e., the shear modulus becomes progressively higher with increasing φ_o. A linear increase in G with φ_o is expected from classical rubber elasticity theory,[93] but the observed increase of G in Fig. 7(b) is clearly not linear in φ_o. This non-linear variation of G on φ_o has been observed in many previous studies of solution cross-linked gels, and there have many efforts to account for this important effect. Shibayama and co-workers[93] reviewed earlier observations on $G(\varphi_o)$ and made a quantitative study of the non-linear concentration dependence of G on φ_o in well-characterized hydrogels formed by cross-linking four-arm polyethylene glycol star precursor polymers in solutions where G was found to scale as $G \sim \varphi_o^{1.51}$ for φ_o larger than a critical value φ_o^* at which an elastic polymer network is first observed. Yet again, we emphasize that this exponent is an apparent value, given the limited data range. Nonetheless, this apparent exponent is useful for summarizing the trend in our data, and we report this exponent in the spirit of previous experimental studies of polymer solutions and gels swollen by solvents where the range of data is normally likewise limited. The "critical gelation concentration" φ_o^* where an elastic network was first observed was estimated to be on the order of the
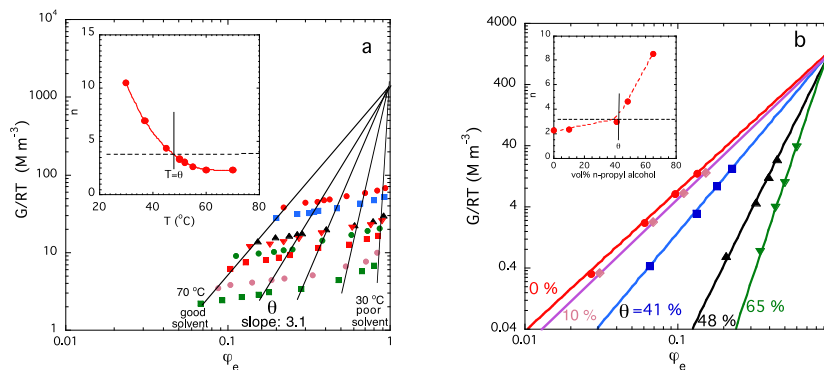
FIG. 6. Reduced shear modulus G/RT vs polymer concentration φ_e plots under equilibrium conditions for PVAc gels in isopropyl alcohol at different T (a) (symbols are the same as in Fig. 2) and for PVA gels in n-propyl alcohol and water mixtures (b). Insets show the variation of the power-law exponents corresponding to the main panel as the solvent quality is varied. Note that G/RT for both PVAc and PVA gels extrapolates to a common "dry" network value, a result that we did not initially anticipate.
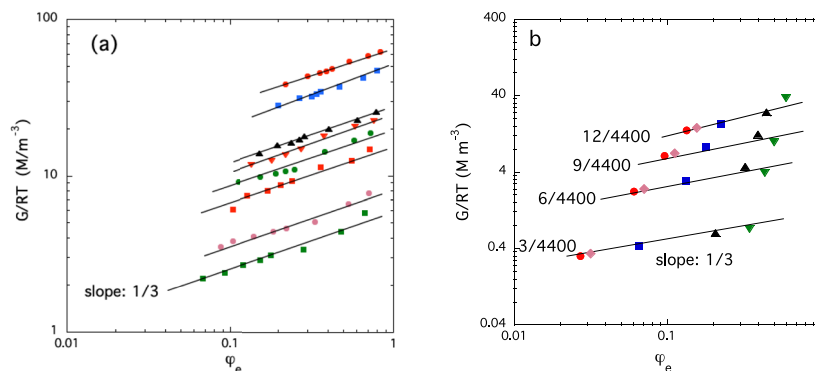

FIG. 7. Reduced shear modulus G/RT vs φ_e at a fixed cross-linking density for PVAc gels in isopropyl alcohol at different T (a) (symbols are the same as in Fig. 2) and for PVA gels swollen in n-propyl alcohol/water mixtures (b). Continuous lines show the variation of G/RT for nominally identical gel samples.

polymer overlap concentration, c^* (see further discussion below). These observations together are consistent with earlier observations on less well-characterized gels[93] and offer significant clues into how the "front factor" of G might be modeled.

After first checking that the scaling of G with φ_o in our PVAc networks is qualitatively consistent with previous observations,[93] we then sought a more quantitative description that accounts for the occurrence of φ_o^*. The formation of a network having finite G at a critical concentration φ_o^* and the observation of a strong non-linear scaling of G with φ_o both suggest to us that a rigidity percolation theory description of this phenomenon that goes beyond a mean field level description is required to understand the φ_o dependence of G. Conveniently for us, Nishi et al.[94] has recently formulated such a model based on similar physical reasoning. We next consider a quantitative check of this physically plausible model.

Nishi et al.[94] approached this difficult problem by considering the simpler problem of decimating an initially perfect idealized model of a network (rigidity percolation is normally formulated on a lattice for reasons of mathematical expediency) by cutting network bonds of the network up to the point at which the network loses it rigidity. This approach was also taken in the molecular dynamics simulation study of the swelling of branched polymer networks by Chremos et al.[25] The reason for this strategy is clear. It is evidently easier to model or simulate the disintegration of the network than its formation. As one generally expects from rigidity percolation modeling, Nishi et al.[94] found that the shear modulus G of the decimated ("defective") network scaled as a power of the fraction p of the intact network bonds minus the critical rigidity percolation fraction concentration p_c at which the shear modulus G of the network first becomes non-zero, i.e., $G/G_o \sim [(p - p_c)/(1 - p_c)]^t$, $p > p_c$ for p near but above p_c. Here, G_o is the shear modulus of the reference "perfect network" without defects where the power theory index t was estimated to be approximately equal to 1.6 for near "critical" networks ($p \approx p_c$) in three dimensions, a limit appropriate for networks formed by lightly cross-linking of semi-dilute polymer solutions where the initial polymer concentration is not that much larger than the critical concentration and the overlap concentration. In the limit of high cross-linking density, where fluctuation effects associated with the rigidity percolations become less prevalent, Nishi

et al. predicted a crossover to the mean field rigidity percolation scaling,[95]

$$G/G_o \sim [(p - p_c)/(1 - p_c)]. \qquad (5)$$

A test of the model of Nishi *et al.* requires an estimation of the lattice parameter p. Following the work of de Gennes,[13] we may imagine the uncross-linked polymer solution to be a "lattice" of touching blob-like chain domains in a coarse-grained sense, so we may plausibly identify the filling fraction p as being proportional to φ_o. We obtain further evidence for this type of non-linear dependence of G on φ_o in the precise study of hydrogels formed from four-arm polyethylene glycol star precursor polymers by Shibayama and co-workers,[93] where G was found to exhibit the apparent scaling, $G \sim \varphi_o^{1.51}$, and they further reported a crossover to the linear scaling of G on φ_o for large values of φ_o. This higher concentration scaling regime is expected from mean field theory and corresponds physically to a regime in which fluctuations in the network topology are relatively small. This crossover in the concentration dependence of G is in good qualitative accord with the expectations of rigidity percolation theory.

Since the fraction of network defects can be expected to be a function of the polymer concentration (polymer mass concentration, c) relative to the polymer overlap concentration c^*, as found in certain model networks,[91] the fraction of network defects can be expected to decrease progressively with the increasing initial polymer concentration, φ_o.[91,96–99] Based on this reasoning, we may now understand the strongly non-linear scaling that we observe between G and φ_o and even the particular scaling exponent and the existence of the observed rigidity percolation concentration φ_o^*, if we take $p \sim c/c^*$ in the rigidity percolation model, where the symbol "~" indicates a relation holding in the sense of order of magnitude so that the prefactor is unspecified. This is the typical situation in scaling theory arguments. Notably, the estimate of c^* itself depends somewhat on the property from which this quantity is estimated (radius of gyration, intrinsic viscosity, and hydrodynamic radius) because flexible polymers are not spheres.

We now have all the required ingredients to have a predictive relation for the topological front factor $A_T \equiv G/RT \, \varphi_e^{1/3}$ of G for solution cross-linked polymer gels,

$$A_T/A_{T,o} \sim [(\varphi_o - \varphi_o^*)/(1 - \varphi_o)]^t, \qquad (6)$$

where t is a percolation theory exponent, which takes a value near 2 for lattice percolation, but which often takes values closer to 1.5 in off-lattice systems (i.e., the exponent is not universal). For example, t has been observed to equal 1.5 and 1.56 in silica and carbon black particle polymer composites[100] and to take values in the range 1.5–1.8 in the elastic plateau modulus of cross-linked actin networks.[101] It was originally predicted by de Gennes that t should take the lattice percolation theory value near $t \approx 2$,[102,103] and this value of t is sometimes reported experimentally.[104] The exponent estimate $t = 1.6$ by Nishi *et al.*[94] is reasonably consistent with the observed range of experimental estimates of this exponent, but it should be appreciated that there is some uncertainty in the value of this exponent that relates to the complexities of rigidity percolation.[103] In Fig. 8, we plot $\log(A_T)$ as a function of $\log(\varphi_o - \varphi_o^*)/(1 - \varphi_o^*)$ for our PVAc gel data and fit these data to Eq. (5) where we find that this expression describes our observations rather well with the
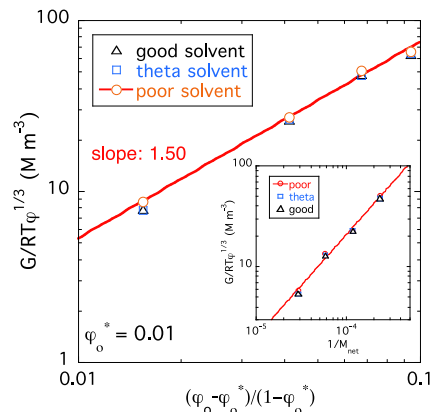

FIG. 8. $G/RT\varphi^{1/3}$ vs $(\varphi_o - \varphi_o^*)/(1 - \varphi_o^*)$ plots for PVAc/isopropyl alcohol gels prepared at constant M_{net} = 4300 Da in a good solvent (70 °C), theta solvent (52 °C), and poor solvent (30 °C). Inset: $G/RT \, \varphi^{1/3}$ vs $1/M_{net}$ plots for PVA and water/*n*-propyl alcohol gels prepared at 9% (m/m) polymer concentration in a good solvent (70 °C), theta solvent (52 °C), and poor solvent (30 °C). The invariance of variation of $G/RT \, \varphi^{1/3}$ with the initial polymer concentration and the molecular mass of the network chains M_{net} (cross-link density) to changes in solvent quality is notable.

parameter values, t = 1.51 and φ_o^* = 0.01. This apparent scaling exponent estimate is consistent with the previous reported observations by Shibayama and co-workers[93] of G scaling φ_o with an exponent 1.51 φ_o^* estimated to be about $\varphi_o^* \approx 0.01$. This is a typical order of magnitude of the polymer overlap concentration in our system as well based on intrinsic viscosity [η] measurements on the precursor PVA chains of our PVAc gels using the overlap concentration estimate, $\varphi_{o,\eta}^* = 1/[\eta]$.[105] The rigidity percolation would appear to provide a good accounting of the dependence of the shear modulus of PVAc gels on the initial polymer concentration. The estimation of the precise value of scaling exponent and the critical concentration is inherently uncertain, given the limited data, and we can at least claim qualitative agreement with former experimental studies and the proposed theoretical framework.

Previous systematic studies for PVAc gels cross-linked in solutions indicate that the front factor of the shear modulus also depends on the molecular mass of the precursor uncross-linked polymers in solutions.[106] In particular, the prefactor under the same nominal initial polymer concentration φ_o and number of cross-links increases with the initial polymer mass, but a saturation to a constant value seems to occur in the limit of large uncross-linked polymer mass. We interpret this trend to arise from the reduction of dangling chain defects in solution cross-linked networks. Our simulation data for the influence on the initial polymer mass on G of the PVAc gels are limited, but there are extensive data for close related hydrogels of PVA that could be analyzed to better understand the influence of this molecular parameter on the elasticity of solution cross-linked gels.[105] We also point out a classic study of the effect of precursor polymer mass dependence of the front factor of G by Mullins[107] for polymer network cross-linked in the dry state where the same general qualitative trend is observed as in our solution cross-linked polymer networks.
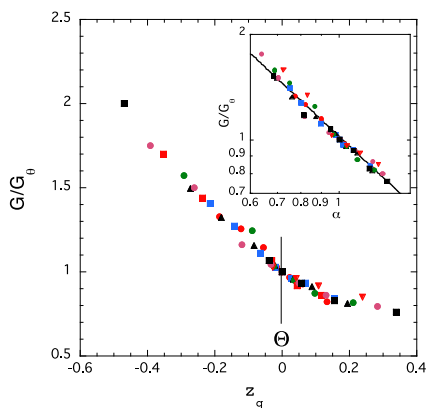
FIG. 9. Reduced shear modulus G by its value at the theta point G_θ as a function of the dimensionless excluded volume interaction parameter z_g for PVAc gels in isopropyl alcohol. Symbols are the same as in Fig. 2. Inset: G/G_θ as a function of α for PVAc gels in isopropyl alcohol. Symbols have the same meaning as in Fig. 2.

We now come to the analysis of the temperature, cross-link density, and initial polymer concentration dependences of G based on a similar reduced variable description as used for network swelling and deswelling in Sec. IV A. In Fig. 9, we see that reducing G by its value at the theta temperature, we reduce all shear modulus data to a near universal function of z_g in both the good and poor solvent regimes. Our reduced variable description of the swelling properties of the PVAc gels evidently extends to the case of the shear modulus. Moreover, the inverse trends of $\alpha(z_g)$ in Fig. 3(b) and G/G_θ in Fig. 9 suggest a specific power law relation between $\alpha(z_g)$ and G/G_θ, and we confirm this expectation in the inset of Fig. 9. We see that G/G_θ scales as $G/G_\theta \sim \alpha(z_g)^{1.17}$ or roughly linearly. We again emphasize that the exponent is only an apparent one, given the limited range and the scatter of the data. There is no question, however, that the gels evidently show a commensurate relative softening as they expand.

V. CONCLUSIONS

Although the problem of swelling and deswelling of polymer gels formed by cross-linking polymers in solutions is a classic problem in polymer science having an enormous number of practical applications, the development of a predictive theory of the influence of variations of "solvent quality" on network dimensions and elastic properties has been slow to develop.

As opposed to theoretical modeling of the swelling of polymers in solutions where many advances have been made to address how fluctuation affects the characteristic of these solutions (e.g., scaling theory, self-consistent field theory and renormalization group theory, direct enumeration and Monte Carlo modeling of lattice polymers, and molecular dynamics simulation), most models of swelling in these materials take the polymers in their melt state in the absence of solvent as the reference state rather than polymers at their theta point, as in the study of polymers in solutions. While this approach is advantageous in some ways for polymer materials in which the solvent concentration is low (less than about 10% by volume) because of the applicability of the mean field Flory Huggins

theory, the treatment of swelling in the dense limit is complicated by strong intrachain interactions that complicate the modeling of the elastic properties of these materials, which is a basic ingredient in modeling swelling of polymer networks based on the Flory–Rehner model. The complete breakdown of the Flory–Huggins theory when polymer networks have swollen to a large degree is another problem with this approach when this type of modeling is applied to networks formed by cross-linking of polymer solutions. Following the work of Zrinyi and Horkay[31,32] and latter arguments by Khokhlov,[69] we approach the problem of describing the solvent quality dependence of polymer networks by the same methodologies as used before for describing the effect of variable solvent quality on the solution properties of flexible polymers in solutions to guide our description of network swelling and deswelling without the invocation of mean field modeling of the excluded volume interaction in these polymers. In particular, our approach to describing network swelling closely follows a molecular dynamics simulation study of polymer networks having variable excluded volume interactions by Chremos *et al.*[25] where the same general type of reduced variable description of network swelling is described in detail and applied to simulated polymer networks having precise controlled topology.

The success of our experimental study of swelling in polymer networks under variable solvent quality conditions relies on the choice of the theta point condition (independently validated) as a reference point for describing network swelling rather than the network in its dry state. The realization of the correct reduced variable description of network swelling also relied heavily on previous theoretical arguments aimed at defining the reduced excluded volume interaction parameter z_g appropriate to network polymers[31,32] and polymer grafted layers[73] where many-body interactions associated with the intrinsically higher segmental densities of these polymer structures must be incorporated into this basic measure of polymer self-interaction, mediated by the solvent. Our analysis also greatly benefitted from the suppression of interchain interactions in deformation properties of polymer networks formed by cross-linking polymers in semi-dilute solutions, as evidenced by the near perfect applicability of classical elasticity to this class of networks, a tremendous simplification of the problem of describing polymer network swelling and changes in network elasticity arising from swelling and the initial polymer concentration at which the networks were formed.[66] Based on this unconventional perspective, we drew upon quantitative theoretical predictions derived from renormalization group theory for the swelling of both linear and randomly branched polymers to deduce a reduced variable description of the solvent quality variation of swelling of network polymers, and this expression is extended to describe the solvent quality dependence of the shear modulus G of solution cross-linked polymer networks by combining scaling relations for network elasticity with classical rubber elasticity theory.

We should note that while we expect our reduced variable description of the swelling, deswelling, and shear modulus of polymer networks cross-linked in semi-dilute solutions to be widely applicable to gels of this kind, it will be necessary to check this scaling description for other gels to establish if this framework provides a "universal" description of these materials.

Clearly, there must be some limitations since polyelectrolyte gels and some solution cross-linked gels in mixed solvents have

been observed to exhibit a nearly discontinuous swelling–deswelling transition that may be approximately described as a first-order phase transition. Dusek and Dušková-Smrčková[58] reviewed this type of abrupt swelling–deswelling or "volume phase transition" phenomenon, which is clearly distinct from the continuous swelling and deswelling that we observe in our PVAc gels when the excluded volume interaction is varied by changing the temperature. We agree with the arguments by Erman and Flory[84] that this alternative type swelling–deswelling transition should become prevalent when ternary interactions become sufficiently prevalent, which in the language of Dusek and co-workers corresponds to the concentration dependent contribution of the apparent Flory–Huggins interaction parameter, χ.[57] Recent work has shown that ternary interaction can become large and variable with salt concentration in polyelectrolyte gels, especially at higher valent ion concentrations in charged polymer networks,[63] which often exhibits this type of abrupt deswelling transition when pH and salt concentrations are varied or electric fields are applied to charged polymer gels cross-linked in solution.[85,108] Hirokawa and Tanaka[108] made the instructive observation that charged N-isopropylacrylamide solution cross-linked gels exhibit a sharp volume phase transition, while the same gel without the ionizable groups did not. A discontinuous swelling–deswelling transition has also been observed in N-isopropyl amide (NIPAM) where the deswelling appears to be induced by the dehydration of the polymer upon heating.[108,109] Thus, in addition to charge being a relevant parameter for understanding the nature of the swelling–deswelling transition, this transition in hydrogels can apparently be influenced by subtle hydrophobicity effects related to the presence of both hydrophobic and polar groups of the polymer. A change of the swelling–deswelling transition of linear polymers has also been observed in simulations and measurements in polymer collapse in relatively stiff polymers,[110,111] and we expect a similar behavior in their network polymer counterparts. Hirokawa and Tanaka[108] attributed the change in the abruptness of the swelling–deswelling transition of N-isopropylacrylamide solution cross-linked gels with ionizable groups to the polymer rigidifying effect of the ionic groups. Molecular stiffness is likely an important parameter implicated in the sharpness of the swelling–deswelling transition of both linear and network polymers, and the impact of chain stiffness on network swelling–deswelling and elastic properties clearly requires further investigation. Non-universality in the deswelling of linear polymers below the theta point has also been observed.[112] This points to the possibility that many-body interactions, which inevitably become enhanced under collapse conditions,[72] could also lead to non-universality in solution cross-linked polymer melts. Previous work has shown that nontrivial variations of A_3 often accompany such "hydrophobic interactions," even though these interactions remain imperfectly understood.[63]

Further experimental studies on well-characterized networks will be required to better understand the material limitations of the scaling description described in the present paper and specifically the universality of the network dimensions on the excluded volume interaction z_g below the theta point and the dependence of A_3 of solution cross-linked polymer networks on molecular parameters, solution parameters, and cross-link density and the influence of A_3 on the abruptness of the gel swelling–deswelling transition.

In the future, we plan to extend our analysis by further study of the effect of the initial length, concentration, and polydispersity of the polymer chains of semi-dilute solutions from which the network is formed to better understand the influence of fluctuations on the network structure near the rigidity percolation threshold. Our preliminary data suggest that these molecular variables clearly impact the prefactor of classical rubber elasticity through their influence on the network topology. Simulations of network formation are clearly warranted to better understand the structure of these networks where again assumptions of mean field models of network formation are avoided. We may anticipate that the solvent quality dependence of the network properties should depend on the solvent quality conditions at which the networks are formed and that the properties of the resulting networks at the time of cross-linking can be "locked-in" as we have found for polymer networks formed in good solvents. A similar effect has been recently discussed in connection with the knotted state of ring polymers being related to the solvent quality conditions at which the chain ends are closed.[113]

Natural rubber materials and their synthetic counterparts are nearly incompressible materials in both their dry and solution states, provided that these materials are well above their glass transition temperatures where the materials can be subjected to large deformation without fracture or failure by some other instability. The small compressibility of these materials has sometimes been considered, but in this work, we adopted the conventional model where compressibility is neglected.

It seems likely to us that compressibility might become important in networks formed from semi-flexible polymers, however, and this is a feature of polymer networks that deserve more consideration in the future in connection with studies of network elasticity in biological materials, which are often comprised of networks of semi-flexible fibers.

It should be noted that polymer networks in solutions often have an osmotic compressibility that varies significantly with solvent quality. The osmotic modulus would be a very interesting quantity to study in future work. Its determination without invoking Flory–Rehner and Flory–Huggins approximations is not so easy, however. We and others have begun to address this problem through molecular dynamics calculations (mentioned in this paper), and these compositional studies, in conjunction with a large body of measurements, should be helpful in developing theory for this important property of networks formed in solutions.

In the future, we plan to address the computation of the osmotic pressure and osmotic compressibility of PVAc networks and make comparison to a wide body of measurement data for these properties. This will require a theoretical effort of calculating the properties in a fashion that does not assume the mean field Flory–Huggins model. As in the case of network swelling and deswelling, we expect that molecular dynamics investigations of the osmotic pressure and the virial coefficients provide invaluable information that should be useful in developing such a theory. In the meantime, we plan to more closely analyze existing gel osmotic data and osmotic compressibility data to understand the phenomenological variation of the second and third virial coefficients on molecular parameters, such as cross-link density and temperature in order to compare with theoretical predictions.[64]

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ferenc Horkay: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing – original draft (equal). **Jack F. Douglas**: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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