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Prediction of Glass-Transition Temperatures for Compatible Blends Formed from Homopolymers of Arbitrary Degree of Polymerization. Compositional Variation of Glass-Transition Temperatures. 5

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ABSTRACT: A model of one-phase mixtures as regular solutions provides the basis of an entropic theory for the prediction of their glass-transition temperatures from pure-component glass-transition temperatures and associated heat-capacity increments. First-order approximations to an initial equation are derived and related to previous equations proposed to describe the composition-dependent glass transition. The phenomenological theory is then applied to the calculation of glass-transition temperatures for one-phase solutions in which the pure components are of arbitrary molecular mass, to give a predictive equation in terms of pure-component chain end and high-polymer glass-transition temperatures and heat-capacity increments. Calculated values of T_g are found to be in satisfactory accord with experimental glass-transition temperatures for an appropriate binary mixture of polymers. Additionally, the experimental dependence of the Wood parameter on degree of polymerization is accounted for.

Introduction

The development of a theory for the prediction of composition-dependent glass-transition temperatures for multicomponent mixtures which manifest single glass transitions is of some fundamental interest and, moreover, has practical merit in connection with their processing conditions and in-service properties. In addition, such a theory might serve to clarify the areas of validity of the diverse relations at present used to describe the phenomenon[1-8] in what is for various reasons a somewhat post hoc manner.

As a preliminary step toward the development of a consistent scheme for the calculation of glass-transition temperatures of compatible mixtures from pure-component properties, the first two papers in this series[9,10] were given over in turn to a preliminary discussion of the form such a scheme might take and a phenomenological thermodynamic theory for one-phase solutions of high polymers. The entropic theory[10] was shown to give values of T_g in close agreement with observed transition temperatures in binary blends of compatible high polymers and to provide as approximations to a central equation several previous relations for the effect. The third and fourth contributions of the series[11,12] have considered the effect of chain ends on homopolymer glass-transition temperatures as a particular problem in the compositional variation of T_g, on the premise that polymers of arbitrary molecular mass can be considered single-phase solutions of chain ends and high polymers. Predicted glass-transition temperatures were found to be in satisfactory agreement with dilatometric, calorimetric, and dielectric values of this property[11] and two first-order approximations to a principal equation were shown to give expressions identical in form with previous relations[13,14] for the effect of degree of polymerization on T_g. Subsequently, the range of comparison between calculated and observed transition temperatures was extended considerably and the relative accuracy of the central relation and the two fundamentally different first-order approximations clarified.[12]

As the theory for composition-dependent glass-transition temperatures has met with a measure of success both for compatible blends of high polymers and for the effect of

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chain ends on T_g for homopolymers, its further exploration seems warranted. In particular, the formalisms for the two problems mentioned above might be usefully combined to provide for the calculation of glass-transition temperatures for compatible blends of arbitrary molecular-mass components from pure-component chain-end and high-polymer properties. This synthesis is presented below as is a survey of leading approximations to a principal entropic expression for glass-transition temperatures in compatible blends and a comparison of theory and experiment for the combined effect of mixing and molecular mass of T_g.

Theory

Phenomenological Entropic Equations for T_g of Compatible Blends. Consider an n-component isobaric mixture at a pressure P and a temperature T. The specific (per unit mass) entropy $S(T, P)$ can be written as the linear sum of pure-component specific entropies S_i weighted by their respective mass fractions M_i and of the specific excess entropy of mixing ΔS_m

$$S(T, P) = \sum_{i=1}^{n} M_i S_i + \Delta S_m \tag{1}$$

As glass transitions in one-phase multicomponent mixtures occur at fixed composition, a model of compatible blends as regular or ideal solutions necessitates that excess mixing entropies are continuous at T_g.[10–12] Therefore, for these solutions, the pure-component entropy sum in eq 1 remains unchanged as the glass-transition is traversed. The choice of pure-component glass-transition temperatures T_{g_i} as reference temperatures for corresponding pure-component entropies and the introduction of pure-component transition increments of specific heat ΔC_{p_i} (approximated as temperature-independent) then lead directly to the predictive equation[10–12]

$$\ln T_g = \sum M_i \Delta C_{p_i} \ln T_{g_i} / \sum M_i \Delta C_{p_i} \tag{2}$$

The upper and lower limits of the sums in eq 2 and related expressions are as given explicitly in eq 1.

To establish connections between the equation above and the form or content of other expressions found or suggested to reproduce composition-dependent glass-transition temperatures, eq 2 is written as

$$\sum M_i \Delta C_{p_i} \ln (T_g / T_{g_i}) = 0 \tag{3}$$

Subsidiary versions of this expression arise from the approximation of the logarithm, in conjunction with or separate from neglect of the differences between pure-component transition increments of heat capacity.

Retention of the first term in an expansion of the logarithm in eq 3 leads to the expression

$$T_g = \sum M_i \Delta C_{p_i} / \sum M_i \Delta C_{p_i} T_{g_i}^{-1} \tag{4}$$

If all heat-capacity increments are taken as identical, eq 4 becomes

$$T_g^{-1} = \sum M_i T_{g_i}^{-1} \tag{5}$$

A single-term expansion such as leads to eq 4 but applied to the ratios T_{g_i}/T_g yields the relation

$$T_g = \sum M_i \Delta C_{p_i} T_{g_i} / \sum M_i \Delta C_{p_i} \tag{6}$$

Use of the heat-capacity-increment approximation reduces eq 6 to

$$T_g = \sum M_i T_{g_i} \tag{7}$$

An additional equation arises if the heat-capacity approximation is used alone in eq 2 to give

$$\ln T_g = \sum M_i \ln T_{g_i} \tag{8}$$

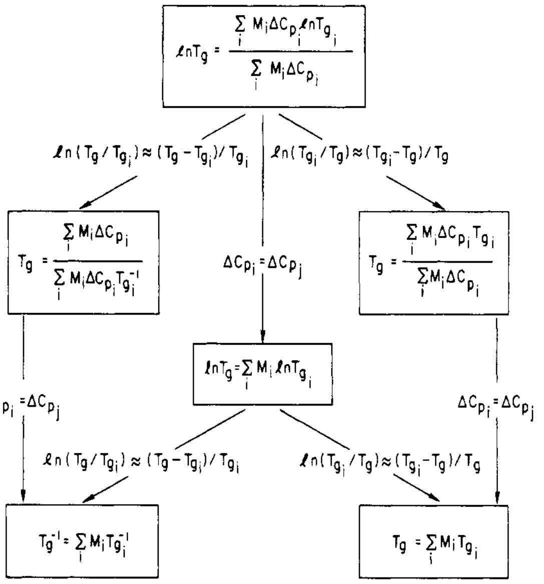

Figure 1. Summary of phenomenological entropic relations for composition-dependent glass-transition temperatures.

The approximations given above and the bases for their derivation from the principal equation are summarized for convenience in Figure 1. As is evident from this summary and from eq 4–7, equivalent orders of approximation can lead to relations fundamentally different in form.

Somewhat separate in principle from the previous relations are those which arise as a consequence of correlations between pure-component glass-transition temperatures and their corresponding heat-capacity increments. For example, use of the empirical rule[15] that for a limited number of polymers the product $\Delta C_{p_i} T_{g_i}$ is approximately constant gives, for eq 4 and 6, in turn

$$T_g = \sum M_i T_{g_i}^{-1} / \sum M_i T_{g_i}^{-2} \tag{9}$$

and eq 5. The latter equation, derived by use of the Simha–Boyer rule, is consistent with the identity $\Delta C_{p_i} T_{g_i} = \Delta C_p T_g$, where T_g is the blend transition temperature and ΔC_p the blend transition increment of heat capacity, predicted by the theory to be

$$\Delta C_p = \sum M_i \Delta C_{p_i} \tag{10}$$

Equation 10 is in satisfactory agreement with the results of experimental measurements of blend transition heat capacities.[16] Relations analogous to eq 9 and 5 can also be written in terms of pure-component heat-capacity increments.

Of the several relations derived in the preceding discussion, eq 4 and 9 are new equations. Both eq 4 and the parallel eq 6 can be rearranged in the form of the Wood[2] equation. However, the respective Wood constants are fundamentally different. As a consequence of this difference subsequent neglect of the variation of the ΔC_{p_i} produces two secondary versions of eq 2 strikingly dissimilar in form: eq 5 is formally identical with the Fox equation,[4] whereas eq 7 gives the blend T_g as the compositional arithmetic mean of pure-component transition temperatures. Neglect of the pure-component heat-capacity variation in eq 2 without a single-term expansion of the logarithmic functions gives an equation for the compositional variation of T_g suggested independently by Pochan, Beatty, and Pochan, on empirical grounds.[7] Finally, appropriate approximation of the logarithmic terms in eq 3 combined with the Simha–Boyer rule gives the second new relation, eq 9, and the Fox equation (again).

For brevity, any detailed assessment of the quantitative adequacy of the various approximations to eq 2 in relation to pure-component properties and experimental measurements of blend glass-transition temperatures is deferred but may well be a suitable topic for inclusion in a later contribution.

Explicit Relations for Blends Formed from Arbitrary Molecular-Mass Components. The previous analysis applied separately to high-polymer mixtures[10] and solutions of arbitrary molecular-mass homopolymers[11,12] readily provides a theoretical equation for blend glass-transition temperatures as functions of pure-component mass fractions and pure-component degrees of polymerization. In effect, the general blend of compatible polymers is modeled as a regular solution of pure-component high polymers and chain ends, in proportions determined by the number-average degree of polymerization particular to each component. From eq 10 (see also ref 11 and 12) the transition increment of heat capacity (per mer) for the ith-component, number-average degree of polymerization n_i is predicted to be a linear sum of high-polymer and dimer increments, distinguished in turn by superscripts $\circ$ and e

$$\Delta C_{p_i} = [(n_i - 2)\Delta C_{p_i}{}^{\circ} + 2\Delta C_{p_i}{}^{e}]/n_i \tag{11}$$

The pure-component glass-transition temperatures can be calculated from dimer and high-polymer glass-transition temperatures (in turn, $T_g{}^e$ and $T_g{}^{\circ}$) and their corresponding increments of specific heat from the equation[11,12]

$$\ln T_{g_i} = \frac{\Delta C_{p_i}{}^{\circ} \ln T_{g_i}{}^{\circ}(n_i - 2) + 2\Delta C_{p_i}{}^{e} \ln T_{g_i}{}^{e}}{\Delta C_{p_i}{}^{\circ}(n_i - 2) + 2\Delta C_{p_i}{}^{e}} \tag{12}$$

Substitution of eq 11 and 12 in eq 2 constitutes a full explicit theoretical relation for the glass-transition temperatures of compatible blends in terms of pure-component high-polymer and dimer glass-transition properties.

As those dimer properties required by the theory will not invariably be available, the replacement of these by "generalized" chain-end transition properties is outlined below. If the lowest number-average degree of polymerization for which reliable data are available for component i is denoted as k_i, the pure component is modeled as a compatible mixture of mers with properties of the low-molecular-mass component (these properties denoted by superscript k_i) and mers with properties of the high polymer. The transition increment of heat capacity (per mer) for a homopolymer of degree of polymerization n_i is (cf. eq 10)

$$\Delta C_{p_i} = [(n_i - k_i)\Delta C_{p_i}{}^{\circ} + k_i \Delta C_{p_i}{}^{k_i}]/n_i \tag{13}$$

with a glass-transition temperature given by

$$\ln T_{g_i} = \frac{\Delta C_{p_i}{}^{\circ} \ln T_{g_i}{}^{\circ}(n_i - k_i) + k_i \Delta C_{p_i}{}^{k_i} \ln T_{g_i}{}^{k_i}}{\Delta C_{p_i}{}^{\circ}(n_i - k_i) + k_i \Delta C_{p_i}{}^{k_i}} \tag{14}$$

There is an element of redundancy in the preceding development, as within the context of the present theory $\Delta C_{p_i}{}^{k_i}$ can be separated into dimer and high-polymer contributions and the dimer glass-transition temperature can then be calculated. However, such a decomposition may be neither advantageous nor practicable and, therefore, the dimer and generalized-chain-end descriptions might be viewed as separate in spirit.

The various chain-end (in the dimer or generalized sense) and high-polymer transition temperatures and their corresponding transition increments of heat capacity are necessary for the combined use of eq 2, 13, and 14: $4n$ data in all. If there are q solely high-polymer components, $2(2n - q)$ data suffice.

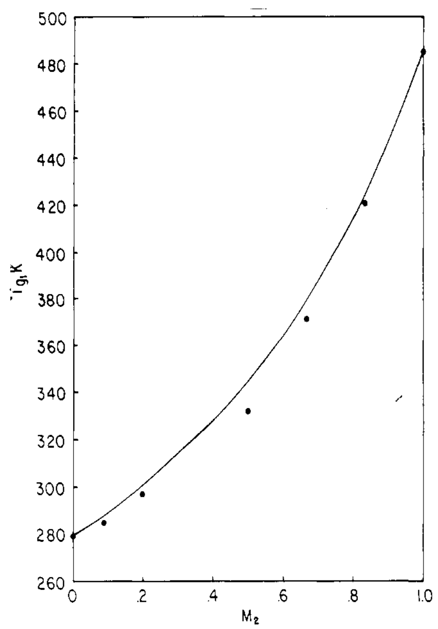

Figure 2. Predicted and experimental glass-transition temperatures for a blend of high-polymer PPO with oligomers of PS. The full line is calculated from eq 2, 13, and 14 as discussed in the text. Experimental transition temperatures[18] are shown as filled circles.

Comparison between Theory and Experiment

Blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) have been found to give several indications of compatibility for high-polymer components.[17] These indications include direct measurements of negative enthalpies of mixing, sufficient but not necessary for single-phase mixtures. Studies of transition behavior in high-polymer blends of PPO with monodisperse PS of various degrees of polymerization (from the oligomer to high-polymer range) also exhibit properties consistent with compatibility.[18] In particular, their quenched (amorphous) blends were found to manifest composition-dependent single glass transitions and are therefore assumed to provide data acceptable for a critical test of the theory embodied by eq 2, 13, and 14.

For the calculation of glass-transition temperatures in blends of high-polymer PPO with various polystyrenes from the appropriate chain-end and high-polymer properties, glass-transition temperatures and heat-capacity increments are available for PS chain ends, and for high polymers of both components. To afford a consistent comparison between calculated and experimental glass-transition temperatures the properties of the lowest molecular-mass PS component used in the study by Kwei and Frisch[18] (an oligomer) are used and, where possible, pure-component properties for PPO and PS are also those reported there. Thus for PS $k_1 = 8$ with the oligomer glass-transition temperature $T_{g_1}{}^8 = 279$ K, and the high-polymer glass-transition temperature $T_{g_1}{}^{\circ} = 373$ K. The PPO high-polymer glass-transition temperature is $T_{g_2}{}^{\circ} = 485$ K. Transition increments of heat capacity for PS are[19] $\Delta C_{p_1}{}^{\circ} = 0.0671$ cal g^{-1} K^{-1} and $\Delta C_{p_1}{}^{e}/\Delta C_{p_1}{}^{\circ} = 2.05$[20] to give (from eq 11) $\Delta C_{p_1}{}^{8} = 0.0847$ cal g^{-1} K^{-1}. For PPO[19], $\Delta C_{p_2}{}^{\circ} = 0.0528$ cal g^{-1} K^{-1}. Predicted (eq 2, 13, and 14) and observed glass-transition temperatures for the PPO/PS blends investigated by Kwei and Frisch are compared in Figures 2–5. The temperature of initial rise of heat capacity was taken as the glass-transition temperature for

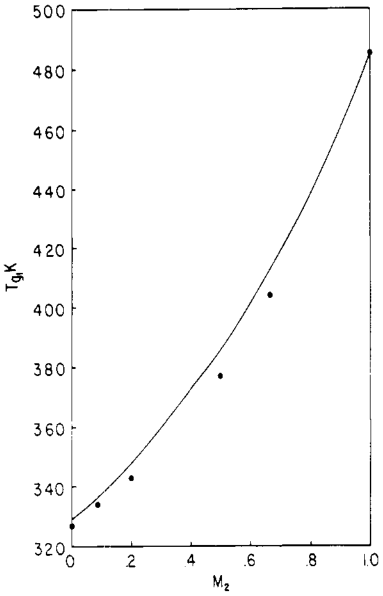

Figure 3. Predicted and experimental glass-transition temperatures for a blend of high-polymer PPO with PS, degree of polymerization 21.2. The full line is calculated as described for Figure 2. Experimental transition temperatures[18] are shown as filled circles.

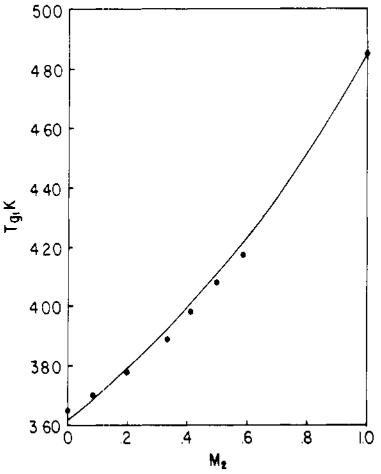

Figure 4. Predicted and experimental glass-transition temperatures for a blend of high-polymer PPO with PS, degree of polymerization 96.2. The full line is calculated as for Figures 2 and 3. Experimental transition temperatures[18] are shown as filled circles.

blends and their pure components, at a consistent heating rate of 20 °C min^{-1}. Further experimental details are given in the original report.[18]

As illustrated by Figures 2–5, theory and experiment are in satisfactory agreement. A small composition-dependent difference between the two is evident and can be accounted for in sign and magnitude by the effect of composition-dependent glass-transition broadening in conjunction with the particular experimental convention used to define T_g. This explanation is supported, at least indirectly, by the observation that use of the transition midpoint convention for T_g gives experimental and theoretical transition temperatures within experimental error for high-polymer blends of PPO and PS.[10] There is an additional possible source of disagreement between theory and experiment consequent on the use of the chain-end transition increment of heat capacity for thermally polymerized rather than for anionically polymerized PS in default of information on the latter. However, as shown in a previous paper,[11] close agreement between the predicted and observed effect of degree of polymerization on T_g for PS arises if this substitution is made. The relatively small difference between the nature of end moieties for anionic and thermal PS and the second-order nature (physically) of the transition heat-capacity effect are consistent with any associated differences as may occur, being relatively minor.

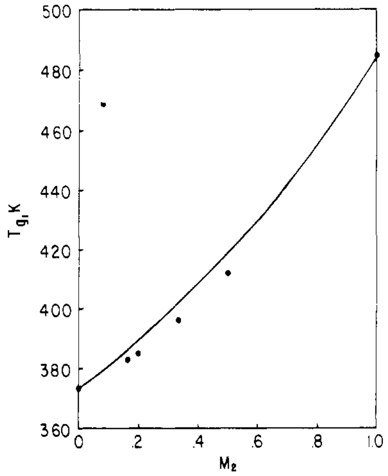

Figure 5. Predicted and experimental glass-transition temperatures for a blend of high-polymer PPO with PS, degree of polymerization 355.8. The full line is calculated as for Figures 2–4. Experimental transition temperatures[18] are shown as filled circles.

Kwei and Frisch showed that their data could be reproduced acceptably by a relation of the form

$$T_g = (M_1K_1T_{g_1} + M_2T_{g_2})/(M_1K_1 + M_2) \qquad (15)$$

where K_1 is a characteristic constant for each blend. The Wood-type predictive equation for binary blends is, from eq 4 and 6, in turn

$$T_g = \frac{M_1(\Delta C_{p_1}T_{g_2}/\Delta C_{p_2}T_{g_1})T_{g_1} + M_2T_{g_2}}{M_1(\Delta C_{p_1}T_{g_2}/\Delta C_{p_2}T_{g_1}) + M_2} \qquad (16)$$

and

$$T_g = \frac{M_1(\Delta C_{p_1}/\Delta C_{p_2})T_{g_1} + M_2T_{g_2}}{M_1(\Delta C_{p_1}/\Delta C_{p_2}) + M_2} \qquad (17)$$

Substitution of explicit expressions for the effect of chain ends on pure-component glass-transition temperatures and heat-capacity increments gives a basis for the prediction of Wood constants from pure-component properties. When component 2 is a high-polymer, the Wood parameter from eq 16 is

$$K_1 = \frac{\Delta C_{p_1}{}^{\circ}T_{g_2}{}^{\circ}}{\Delta C_{p_2}{}^{\circ}T_{g_1}{}^{\circ}}\left\{1 + \frac{2}{n_1}\left(\frac{\Delta C_{p_1}{}^{e}T_{g_1}{}^{\circ}}{\Delta C_{p_1}{}^{\circ}T_{g_1}{}^{e}} - 1\right)\right\} \qquad (18)$$

and, in an analogous fashion, from eq 17

$$K_1 = \frac{\Delta C_{p_1}{}^{\circ}}{\Delta C_{p_2}{}^{\circ}}\left\{1 + \frac{2}{n_1}\left(\frac{\Delta C_{p_1}{}^{e}}{\Delta C_{p_1}{}^{\circ}} - 1\right)\right\} \qquad (19)$$

Both eq 18 and eq 19 are equivalent in form to the dependence of K_1 on n_1 found experimentally for PPO/PS blends and rationalized on the basis of a free-volume contribution due to chain ends.[18]

The most critical relative test of eq 16 and 17 and their further explicit forms results from a comparison of calculated and reported values of K_1 for blends with widely separate pure-component glass-transition properties and for which T_g data is well fit by the form of eq 15. For PPO blended with PS oligomers, the pure-component glass-transition temperatures differ by >200 K, and the value $K_1 = 2.50$ reproduces blend transition temperatures to within 5 K.[18] Equations 16 and 17 give, respectively, $K_1 = 2.79$ and $K_1 = 1.60$. Thus, although strictly the difference between pure-component glass-transition temperatures might seem rather large for the single-term expansions necessary for eq 16 and 17, the former is the more acceptable for compatible blends of PPO and PS (for which $\Delta C_{p_2}/\Delta C_{p_1} < 1$) and, indeed, is fairly accurate.

Final Remarks

A phenomenological theory for the compositional variation of glass-transition temperatures in one-phase mixtures based on a model of these as regular solutions has now been shown to account with some success for the phenomenon in binary mixtures of high polymers and, also, to give an acceptable description of the variation of glass-transition temperatures with molecular mass for homopolymers. Further, as described in the present contribution, these two formal treatments can be combined to predict glass-transition temperatures in compatible blends of arbitrary composition and pure-component degree of polymerization from component chain end and high-polymer glass-transition temperatures and their reciprocal heat-capacity increments, equivalent to the generation of a $2n$-dimensional surface.

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The Poisson Ratio in Polymer Gels

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ABSTRACT: A comparison is made between the longitudinal elastic modulus and the shear modulus in polyacrylamide gels. The former is measured by inelastic light scattering as well as by osmotic deswelling; the latter is measured by observation of the frequency of standing waves excited in the samples. The ratio of these two quantities is found, within experimental error, to be equal to 2 in a poor solvent (1:3 methanol–water at 11.5 °C), as is to be expected from the Gaussian nature of the polymer chains in Θ conditions (the Poisson ratio σ of the polymer coils is equal to zero). In a good solvent, a scaling argument based on the Flory expression for the free energy predicts that $\sigma = {}^1/_4$. The experimentally measured values are significantly larger and increase as the quality of the solvent improves.

I. Introduction

When solvent is removed from a polymer solution or a gel, there is an accompanying increase in the osmotic pressure, the magnitude of which defines the osmotic elastic modulus of the medium. In the semidilute region the elastic modulus follows a scaling law as a function of polymer concentration c: it is proportional to c^a, where the exponent a is 2.25 in a good solvent[1] and equal to 3 in a Θ solvent.[2] These theoretical predictions have been confirmed by neutron scattering measurements of the coherence length in polymer solutions,[3,4] by direct mechanical measurements on gels in a good solvent,[5,6] and by inelastic light scattering for gels in a poor solvent.[7]

In each of the above theoretical and experimental investigations it is assumed that there is no behavioral distinction between the osmotic bulk modulus K and the shear modulus μ (or any combination of the two, such as the longitudinal elastic modulus $E = K + 4\mu/3$). Although it might seem surprising that μ, which describes a deformation unaccompanied by a change in solvent concentration, should be related to the osmotic pressure, this must nonetheless be so: both K and μ are related in the same way to the tension acting on the polymer chains and the number of tie points in the network. Candau et al.[8] have recently been able to demonstrate this property by showing that the variation of E deduced from light scattering measurements on polystyrene–benzene gels (good-solvent conditions) follows closely variations in μ.

In contrast with the above results, the present authors have previously found that in the system polyacrylamide–water E and μ, measured, respectively, by light scattering and mechanical methods, apparently enjoy different types of behavior with concentration. It was

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