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Notes

Elastic Properties of a Polymer Chain with Excluded Volume: A Renormalization Group Theory

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The elastic behavior of a single polymer chain in a good solvent is related to a number of important problems, including the general problem of rubber elasticity of swollen networks. This behavior has been studied recently by using scaling arguments[2] and by Monte Carlo methods.[3] The scaling arguments can describe the elastic behavior only in the weak and strong stretching regimes; they cannot give information about the intermediate stretching regime, the crossover behavior. The intuitively appealing blob arguments do not work in this interesting crossover regime. The Monte Carlo calculations of Webman et al.[3] describe the response of a single chain to the whole range of the strength of stretching forces. The results of Webman et al. are in conformity with the general scaling arguments in limiting cases, and they suggest that the crossover behavior is fairly abrupt (see Figure 2 of ref 3).

This note provides for the first time the renormalization group calculation of the full range of elastic behavior, including crossover, for a polymer of fixed degree of polymerization with well-developed excluded volume.

In the presence of a stretching force $\mathbf{F}$, the end-to-end vector $\mathbf{R}$ distribution function $f_{\mathbf{F}}(\mathbf{R})$ is proportional to $f(\mathbf{r}) \times \exp(\beta \mathbf{F} \cdot \mathbf{R})$, where $\mathbf{r} = \mathbf{R}/R_0$, $R_0 = \langle R^2 \rangle^{1/2}$ is the root-mean-square end-to-end distance without external forces, $f(\mathbf{r})$ is the end-to-end vector distribution for $\mathbf{F} = 0$, and $\beta = 1/kT$. We have calculated $f(\mathbf{r})$ to order $\epsilon = 4 - d$, d being the spatial dimension, in a preceding paper,[4] using a renormalization group approach with dimensional regularization which is formulated in chain configuration space in terms of full chain distribution functions. These calculations yield[4]

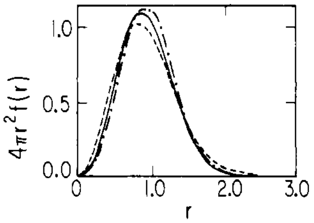

Figure 1. Distribution function for the magnitude of the end-to-end vector $|\mathbf{r}|$ in 3-space: (- - -) denotes the Gaussian distribution function, i.e., the distribution function for a simple random walk; (–·–) estimate of the distribution function for a self-avoiding walk on the simple cubic lattice;[5] (—) distribution function for a self-avoiding random walk from eq 2.

$$f(\mathbf{r}) = \left(\frac{2}{\pi}\right)^{2-\epsilon/2} 2^{\epsilon/8} \exp\left(\frac{1}{8}\epsilon\hat{\gamma} - \frac{3}{4}\epsilon\right) \times |\mathbf{r}|^{\epsilon/4} \exp\left[-(2\mathbf{r}^2)^{1+\epsilon/8}\left(1 - \frac{3}{8}\epsilon\right) + \frac{\epsilon}{4}(1 - \hat{\gamma})\mathbf{r}^2\right] \quad (1)$$

where $\hat{\gamma} \simeq 0.577...$ is Euler's constant. In 3-space the correctly normalized $f(r)$ is given by

$$f(r) = 0.33|\mathbf{r}|^{0.25} \exp(-1.5|\mathbf{r}|^{2.25} + 0.1|\mathbf{r}|^2) \quad (2)$$

The function $4\pi r^2 f(r)$ is compared in Figure 1 to the estimation obtained by Domb et al.[5] The agreement is good

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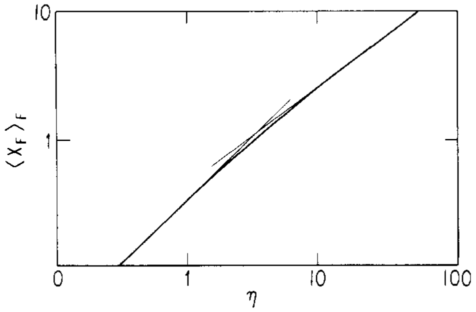

Figure 2. Plot of $\langle X_F \rangle_F$ vs. η in 3-space, where $\langle X_F \rangle_F = \langle \mathbf{R} \cdot \mathbf{F} \rangle_F / R_0 |\mathbf{F}|$ and $\eta = |\mathbf{F}| R_0 / kT$. Note that the crossover range is very wide.

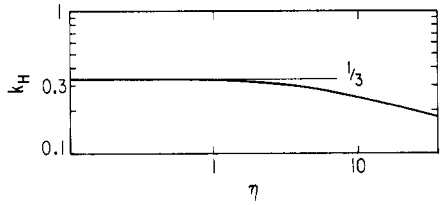

Figure 3. Plot of the effective Hooke constant $k_H = kT \langle \mathbf{R} \cdot \mathbf{F} \rangle_F / |\mathbf{F}|^2 R_0^2$ vs. η in 3-space. k_H is $^1/_3$ in the weak-force limit. It deviates significantly from $^1/_3$ for $\eta \gtrsim 1$.

and is expected to be almost perfect if we extend our calculation to order ϵ^2. Even in 2-space ($\epsilon = 2$), eq 1 displays the correct qualitative features.

The distribution function (2) can be used to calculate the average of the component $R_F \equiv \langle \mathbf{R} \cdot \mathbf{F} \rangle_F / |\mathbf{F}|$ of $\mathbf{R}$ parallel to $\mathbf{F}$, where $\langle \ \rangle_F$ denotes the average over the ensemble $f(\mathbf{r}) \exp(\beta \mathbf{F} \cdot \mathbf{R})$ with the external force $\mathbf{F}$ imposed. $X_F \equiv R_F / R_0$ is given as a function of $\eta = \beta |\mathbf{F}| R_0$ in Figure 2. The effective Hooke constant $k_H = kT \langle \mathbf{R} \cdot \mathbf{F} \rangle_F / |\mathbf{F}|^2 R_0^2 \equiv \langle X_F \rangle_F / \eta$ is given in Figure 3. In the weak-force limit $\mathbf{F} \rightarrow \mathbf{0}$, $\exp(\beta \mathbf{F} \cdot \mathbf{R})$ is expanded in $\mathbf{F}$, and the result $k_H = 1/d$ in d-space follows directly from the spherical symmetry of the distribution function $f(\mathbf{r})$. Figures 2 and 3 show that Hooke's law is valid for $\eta \lesssim 0.8$. For $\eta \gtrsim 1$, there is a significant deviation from this linear law. The strongly stretched asymptote is reached at around $\eta \simeq 20$. The crossover region is thus very wide. If there are experimental errors or sampling errors in Monte Carlo calculations, then, as is seen from Figure 2 of ref 3, the crossover region is made to appear narrow, so that the crossover seems abrupt. Our calculation is to order ϵ, so the asymptotic slope for higher η in Figure 2 is 0.75 instead of the scaling result of ~0.66. However, the semiquantitative agreement with the Monte Carlo result is encouraging.

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Preparation of Homogeneous "Living" Polyvinyl Gels with Application to Solvent Purification

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Introduction

In this paper we report on the polymerization of divinylbenzene (DVB) into homogeneous gels containing a significant concentration of residual vinyl groups. Methods are described whereby microsyneresis,[1] commonly observed in the polymerization of DVB, is eliminated. These methods of synthesis, therefore, place no restrictions on overall sample size and yield materials of substantial mechanical strength. The utility of these novel homogeneous polyvinyl macrogels is demonstrated in solvent purification.

Experimental Section

Materials. Divinylbenzene (Matheson Coleman and Bell, practical grade) was washed with 10% NaOH and with distilled water and was stored over molecular sieves at 0 °C. Proton NMR analysis confirmed a monomer composition of 60% DVB and 40% ethylstyrene (ES). The [*m*-DVB]/[*p*-DVB] was reported as 3:1 by the manufacturer. Reagent grade benzene, tetrahydrofuran (THF), 1,4-dioxane, and toluene were dried over molecular sieves. *n*- and *sec*-butyllithiums were diluted in hexane or used as received from Aldrich; concentrations were verified by titration, using the method of Eppley and Dixon.[2]

Gel Synthesis. Reactions were performed at room temperature in sealed, flamed, and argon-flushed Pyrex test tubes. Solvents and monomer were each introduced to the vessel by syringe and mixed. Addition of initiator was followed by a color change from colorless to burgundy brown and subsequent gelation. The reacting solution/gel was left for 24 h and recovered in benzene. During storage in benzene, slow reaction with oxygen terminated the living gels, as indicated by loss of color.

Gelation reactions were conducted in solution over a range of monomer concentrations from 2 to 40% (v/v) and at an initiator concentration of 0.016 M. Varying the [THF]/[I] molar ratio between 0 and 4 in benzene has a dramatic effect on the product obtained. Initiation in the absence of THF leads to slow development of color with subsequent polymerization and gelation dominated by extensive microsyneresis; the opaque gel so produced has little mechanical strength and crumbles upon handling. Addition of initiator to a solution with [THF]/[I] = 4 instantaneously produces a burgundy color followed by rapid homogeneous gelation. The product is a clear uniform gel of superior strength. Varying [THF]/[I] between 0 and 4 results in large changes in reaction time and product characteristics. A value of [THF]/[I] = 4 provides adequate time for mixing prior to gelation and yields a product suitable for application to solvent purification (see below). This gel can be readily cut into serviceable pieces as recovered in the swollen state while also containing a significant concentration of accessible vinyl groups. The conditions for the synthesis of this gel are summarized in Table I. As described in the Discussion, homogeneous gels were also obtained from reactions carried out in a mixed solvent composed of 75% dioxane and 25% toluene (v/v).

Characterization. The gel of Table I was analyzed for accessible vinyl content in the following manner: 1.5 g (dry weight) of 0.5-cm^3-size swollen particles was suspended in toluene, charged with excess *n*-BuLi, and allowed to react under purified argon for 1 week. The presence of available vinyl groups in the gels was evidenced by the appearance of a deep reddish brown color. The solution was then drained and a 250-mL aliquot of a standardized solution of toluene and benzoic acid was added. The activated gel particles turned colorless. Aliquots (50 mL each) of the remaining solution were titrated for benzoic acid content with a standardized solution of methanol and sodium methoxide. Phenophthalein was added as an end point indicator. The titration technique was verified independently on a known solution of benzoic acid in toluene. This method yielded a value of 1.4