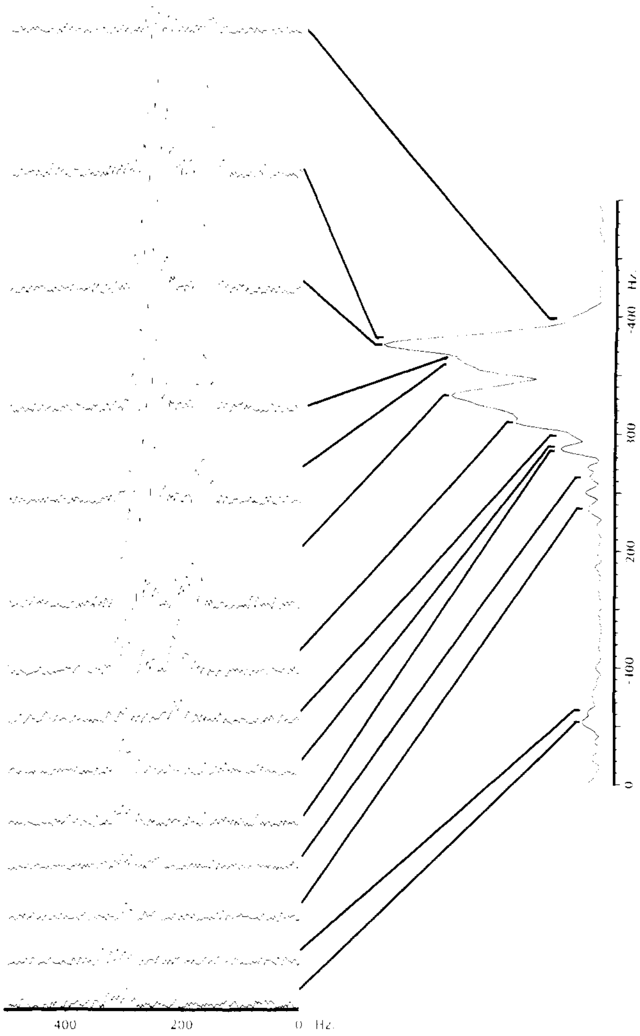

Figure 6. Cross sections in the proton shift dimension of the map shown in Figure 5 taken at the fluorine shift indicated. The spectrum is decoupled in both shift dimensions.

and is surely fast enough to average the chemical shifts of the chemically equivalent protons of the fluorophenyl ring. We did not observe any significant change in the correlation map when the experiment was carried out with a sample temperature of 50 °C, a change that should accelerate phenyl ring rotation. Only two proton chemical shift correlation peaks are expected, therefore, for each unique fluorine chemical shift.

The experiments reported here suggest a large number of magnetically distinguishable environments for the fluorophenyl rings of the polymer. Presumably these correspond to the influence of stereochemical configuration on fluorine shifts. Our maps are not sufficiently resolved to clearly indicate exactly how many of these localized structural possibilities are represented in the correlation map but it is apparent that several fluorophenyl rings with similar fluorine chemical shifts are characterized by detectably different proton shifts. Further work with this system is needed, including the examination of specifically deuterated polymers, before it will be possible to assign the various resonances or correlation peaks observed. A detailed study of the effects of transverse relaxation will also be needed to quantitate the amounts of each of these forms that are present.

Our work to date suggests the power of two-dimensional heteronuclear chemical shift correlations in polymer systems; experiments involving carbon-proton correlations may also be rewarding.

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Registry No. Poly(*p*-fluorostyrene) (homopolymer), 24936-47-8.

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Relationship between Renormalization Group, Two-Parameter Theory and Blob Models of Polymer Excluded Volume

The description of polymer excluded volume has been approached by a variety of different methods, including renormalization group theory,[1] scaling[2] and blob methods,[3-5] the two-parameter theory,[6] and lattice enumeration and Monte Carlo methods. Each is claimed to have a useful range of validity, but the interrelationships between the different approaches have not been established, making it difficult to compare the predictions of the different theories among themselves and, more importantly, with experiment. Here we provide the connections between these diverse methods by considering a wide class of properties of polymers (linear, ring, comb, star, etc. with strands of high molecular weight) at infinite dilution. In addition, we describe some general features of the dependence of these properties on the strength of the excluded volume interaction and on the molecular weight.

The renormalization group provides the natural framework for viewing all of these theories because it is a general method for analyzing the analytic structure of the dependence of polymer properties on excluded volume and chain length. We center on those polymer properties P like hydrodynamic non-free-draining and equilibrium radii, virial coefficients, average Oseen tensor elements, etc., which in the two-parameter theory[6] scale as

$$P = C_p n^{p/2} f_p(z), \qquad f_p(0) \equiv 1 \tag{1}$$

where n is the number of statistical segments, z is the traditional dimensionless z parameter, C_p is a known constant, and f_p is a unknown scaling function that may contain other parameters like intersegment distances along the chain. We will show elsewhere[7] that the renormalization group predictions for P through second order[1] in $\epsilon = 4 - d$, with d the spatial dimensionality, have the general form

$$P = C_p N^{p/2} (2\pi N/L)^{p[2\nu(\eta)-1]/2} F_p(\eta), \qquad F_p(0) \equiv 1 \tag{2}$$

where N is the chain length, η is a crossover scaling variable[8] ranging from $\eta = 0$ in the Gaussian limit to $\eta = \infty$ in the good solvent limit, L is a phenomenological length scale which is compared below to a similar variable that arises in the blob theory, F_p is a scaling function which in second order has the form[1]

$$F_p(\eta) = 1 + a_p \eta (1 + \eta)^{-1} + b_p \eta^2 (1 + \eta)^{-2} \tag{3}$$

for most properties (for viral coefficients the zero-order term involving unity in (3) is absent), and $\nu(\eta)$ is an "effective exponent" in the crossover region between the Gaussian and good solvent limits. To second order we have[1,9,10] ($d = 3$)

$$2\nu(\eta) - 1 = \frac{1}{8}\,\frac{\eta}{1 + \eta}\left(\frac{2\pi N}{L}\right)^{-1/4(1+\eta)} + \frac{15\eta}{256(1 + \eta)} \tag{4}$$

Once $\nu(\eta)$ has been calculated for one property (see ref 1), then the essence of the renormalization group calculation for the properties P is to obtain the prefactor coefficients a_p and b_p. This may be accomplished approximately, as discussed below, if two-parameter calculations are available for $d = 3$. The renormalization group variable η is also related below to a quantity more akin to z of the two-parameter theory.

We now compare eq 2 to the blob theory in the good solvent limit and to the two-parameter theory in poor solvents, since these two theories are generally valid in these limits, respectively. For comparison we consider the $\eta \to \infty$ limit of (2), which is

$$P_{\eta\to\infty} = C_p N^{p/2} (2\pi N/L)^{p(2\nu-1)/2} F_p(\infty) \tag{5}$$

where $\nu \equiv \nu(\eta = \infty)$ and $F_p(\infty) = 1 + a_p + b_p$ to second order. This is to be compared with the good solvent limit blob theory[11]

$$P(\text{blob}) = C_p N^{p/2} (n/n_\tau)^{p(2\nu-1)/2} F_p(\text{blob}) \tag{6}$$

with n_τ the blob size. Hence, we have the correspondence $n_\tau \equiv L/2\pi l$ and $F_p(\text{blob}) = F_p(\infty)$, with $nl \equiv N$ and l a Kuhn length. For example, using the second-order $d = 3$ exponent ν in the blob theory and considering $P \to \alpha_S$, we have $F_p(\text{blob}) = 0.930$, to be compared with $F_p(\infty) = 1 + a_p = 0.929$. ($b_p$ is suspected to be small and this is shown to be the case for $\langle \mathbf{R}^2 \rangle$.[1]) Other properties generally give F_p factors agreeing within 15%, where the renormalization group results are generally known only to first order. There have been a number of proposals for interpolating the blob theory through the crossover region,[3,12,13] but these are somewhat arbitrary. The renormalization group theory (2) provides a systematic description of this crossover region where η is a phenomenological variable,[8] which is easily determined from the penetration function. This η can be used to predict other properties.

In the poor solvent limit η is small, and we will show elsewhere[7] that the renormalization group predictions (2) reduce there to those of the two-parameter theory apart from small numerical differences in a_p and b_p coming from the ϵ-expansion technique. These results are obtained by taking the small excluded volume limits[14] ($d = 3$)

$$\eta \to 32\bar{z}/3 \quad \text{as } \bar{z} \to 0 \tag{7a}$$

$$(2\pi N/L)^{[2\nu(\eta)-1]} \to (1 + 32\bar{z}/3)^{1/4} \quad \text{as } \bar{z} \to 0 \tag{7b}$$

where $\bar{z}$ is a phenomenological variable, playing the same role as z of the two-parameter theory and defined such that $\alpha_{R^2} = 1 + 4\bar{z}/3 + \ldots$ as $\bar{z} \to 0$. Introducing (7) into (2) gives the small-$\bar{z}$ limit to order $\bar{z}$ ($d = 3$)

$$P \to C_p N^{p/2}\left[1 + \frac{32}{3}\left(\frac{p}{8} + a_p\right)\bar{z} + \mathcal{O}(\bar{z}^2)\right] \tag{8}$$

The first-order renormalization group predictions for the coefficients of $\bar{z}$ for $\alpha_S{}^2$ and $h(z)$ are 1.22 and −2.97, respectively.[7,9] These are very close[15] to the two-parameter theory results of 1.28 and −2.87.[6] Hence, in the absence of renormalization group calculations, two-parameter theory calculations to order z can be compared with (8) to provide a good approximation to a_p. (Similarly, the coefficient b_p may be obtained from $\mathcal{O}(z^2)$ calculations, but these are few in number.) Equation 8 provides the stated relation between the renormalization group predictions and the two-parameter theory in the poor solvent regime with the correspondence $\bar{z} \leftrightarrow z$. The importance of this correspondence lies, however, in the fact that (2) may be converted to the $\bar{z}$ representation throughout the crossover domain.[7]

The general renormalization group description of (2) for $p \neq 0$ shows that the crossover regime has two scaling variables,[1] so a universal representation of P in terms of $\bar{z}$ is not possible. However, we have found[7] that this nonuniversality is rather weak and have shown that (2) may be converted into two universal functions of $\bar{z}$ valid in the small- and large-$\bar{z}$ regions

$$P = C_p N^{p/2} (1 + 32\bar{z}/3)^{p/8} [1 + (32/3) a_p \bar{z}/(1 + 32\bar{z}/3)], \qquad \bar{z} < 0.15 \tag{9a}$$

$$P = C_p N^{p/2} (6.441\bar{z})^{p(2\nu-1)} (1 + a_p), \qquad \bar{z} > 0.75 \tag{9b}$$

with[1] $\nu = 0.592$ to $\mathcal{O}(\epsilon^2)$ in $d = 3$. Equation 9a appears to interpolate well[7] between $0.15 < \bar{z} < 0.75$, but it must be tested further in this region.[16] Note that (9) contains only the first-order perturbation coefficient a_p, which may also be obtained approximately from two-parameter theory calculations. However, the renormalization group analysis effectively "resums" the asymptotic perturbation expansion to provide the closed forms (2) or (9).

The renormalization group theory can be extended to describe the concentration[17] and excluded volume[18] dependence of polymer properties. We can, in principle, apply a similar analysis to quantities that scale in the two-parameter theory as $C_p n^{p/2} c^q F_{pq}(z)$, with c the concentration. However, most properties have a more complicated dependence on c through the semidilute region, so this problem should be considered further when more renormalization group calculations for the semidilute region have been performed.

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Entanglement Concepts and Drawing of Polyethylene

In a recent study on ultradrawing of high molecular weight polyethylene[1] we arrived, in our view, unambiguously at the conclusion that the deformation behavior of this polymer at elevated temperature is dominated by the number of trapped entanglements. Very strong evidence for this concept was thought to be the finding that the maximum draw ratio $\lambda_{\max}$ of ultrahigh molecular weight polyethylene (UHMWPE) rapidly crystallized from solutions containing various amounts of polymer depended on the initial polymer volume fraction ϕ as

$$\lambda_{\max} = \lambda_{\max}^1 \left(\frac{1}{\phi} \right)^{1/2} \tag{1}$$

Here, $\lambda_{\max}^1$ refers to the maximum draw ratio of melt-crystallized material. This experimental result could readily be explained in terms of network deformation theories, assuming that the trapped entanglements act as permanent cross-links on the time scale of the drawing experiments. Classical rubber elasticity[2] teaches us that the maximum draw ratio of a cross-linked network is given by

$$\lambda_{\max} = {N_c}^{1/2} \tag{2}$$

where N_c is the number of statistical chain units between cross-links. The corresponding number of statistical chain elements between entanglements N_e in polymer solutions is known[3] to depend on the polymer volume fraction as

$$N_e^{\mathrm{sol}} = N_e^{\mathrm{melt}} \phi^{-1} \tag{3}$$

Substitution of relation 3 in the appropriately modified equation (2) leads to (1) with $\lambda_{\max}^1 = (N_e^{\mathrm{melt}})^{1/2}$. The correct volume fraction dependence of the maximum draw ratio of the UHMWPE films[1b] indicated that all entanglements existing in melt or solution were trapped during the solidification process. Since we used ultrahigh molecular weight polyethylene ($\bar{M}_w = 1.5 \times 10^6$) and quenched the various samples to room temperature, this seems to be plausible.

In this communication we report some results obtained on drawing films of UHMWPE that were produced by careful solution crystallization at various temperatures, i.e., under conditions where chain disentangling during crystallization may occur.

Solutions containing 3% (v/v) of high molecular weight polyethylene ($\bar{M}_w = 3.5 \times 10^6$, Hostalen GUR 412) in decahydronaphthalene were prepared according to previously described procedures[1] at 160 °C and subsequently stored under nitrogen at 79.5, 85.0, 90.5, and 91.5 °C or quenched to room temperature. After completion of the solidification (time lapses indicated in Table I) the obtained gels were dried at ambient conditions. As noted before,[1c] reduction of the thickness of the gels due to solvent evaporation occurred predominantly perpendicular to the film. This dimensional change therefore[4] does not affect the properties in the direction of the films, i.e., the direction of draw. The dried gel films were characterized by differential scanning calorimetry. The heat of fusion, ΔH_f, and the crystallinity, based on $\Delta H_f(100\%) = 293$ J/g, are presented in Table I. These results show the usual, well-documented[5] increase in ΔH_f with increasing crystallization temperature.

Drawing of the dried films was carried out with an Instron tensile tester equipped with a temperature-regulated environmental chamber. A relatively low draw temperature of 90 °C was chosen to prevent excessive disentangling through chain slippage in the drawing process.[1b] The

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