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

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

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

$$\lambda_{\max} = N_{\mathrm{c}}^{1/2} \qquad (2)$$

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

$$N_{\mathrm{e}}^{\mathrm{sol}} = N_{\mathrm{e}}^{\mathrm{melt}}\phi^{-1} \qquad (3)$$

Substitution of relation 3 in the appropriately modified equation (2) leads to (1) with $\lambda_{\max}^{1} = (N_{\mathrm{e}}^{\mathrm{melt}})^{1/2}$. 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 ($\bar{M}_{\mathrm{w}} = 1.5 \times 10^6$) 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 ($\bar{M}_{\mathrm{w}} = 3.5 \times 10^6$, 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 $\Delta H_{\mathrm{f}}(100\%) = 293$ 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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Table I
Preparation and Properties of Films of UHMWPE[a]

T_c, °C	time	ΔH_f, J/g	crystallinity, %
quenched to 25 °C		170	58
79.5	15 h	226	77
85.0	24 h	228	78
90.5	3 days	238	81
91.5	7 days	246	84

[a] Gelation/crystallization from 3% (v/v) in decahydronaphthalene.

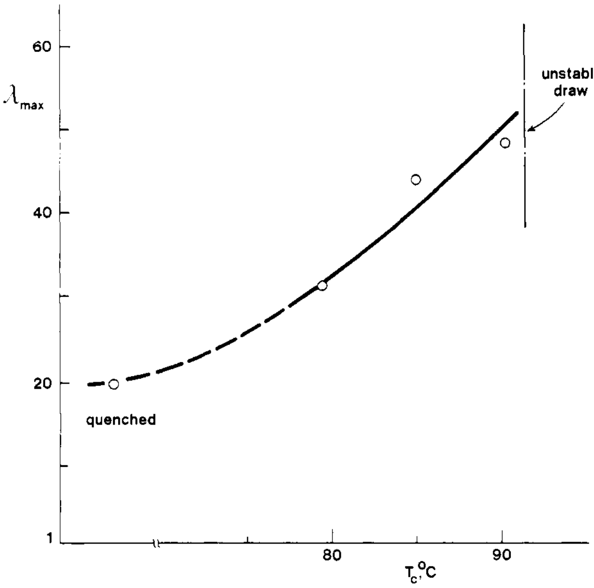

Figure 1. Maximum draw ratio at 90 °C of UHMWPE films produced by gelation/crystallization from a 3% (v/v) solution in decahydronaphthalene at various temperatures.

elongation rate was 100 mm/min and the initial specimen length was 20 mm. The maximum draw ratio was determined in the usual way by measuring the displacement of ink marks printed onto the samples prior to drawing.

For the quenched films we measured a maximum draw ratio of 20. This value is very close to the one calculated with relation 1: $\lambda_{max} = 3.7(0.03)^{-1/2} = 21.4$ ($\lambda_{max}^1 = 3.7$ was obtained previously[1b]). The values for the maximum draw ratio of the various samples are plotted against the crystallization temperature in Figure 1. The graph reveals the dramatic increase of λ_{max} with increasing T_c up to 91 °C. Following the arguments presented above, this result can be understood readily in terms of disentangling during slow crystallization at elevated temperatures and, in fact, provides (indirect) evidence for this phenomenon. The increase in λ_{max} from 20 for the quenched solutions to the value of 50 for the gels produced at 90.5 °C points to a reduction of the number of trapped entanglements by a factor of $(50/20)^2 = 6.25$, as follows from eq 2.

It is remarkable that the gel formed at 91.5 °C could not be drawn to very high macroscopic draw ratios. After necking occurred with a high local draw ratio (~65), the drawn section failed in a fibrillar mode. Apparently, the macromolecular entanglement network in the sample was no longer continuous due to excessive removal of entanglements during crystallization at the high temperature of 91.5 °C.

It is needless to elaborate on the fact that the improved maximum draw ratio was accompanied by strongly improved mechanical properties of the drawn specimens.[6]

The results on the effect of the crystallization temperature on the drawability of solution-crystallized high molecular weight polyethylene tie in very well with the early results obtained by Capaccio and Ward[7] in drawing of melt-crystallized material. These authors established empirically that the optimum thermal history for medium molecular weight polyethylene ($\bar{M}_w \sim 10^5$) was slow cooling from the melt to 110 °C, followed by quenching to room temperature, to obtain high draw ratios. This treatment was preferred to slow cooling to room temperature or direct quenching from the melt. In the latter case most entanglements are trapped, while in the slowly cooled samples the continuous entanglement network structure is partially disrupted by chain disentangling during crystallization.

The present results provide further evidence that the deformation of polyethylene (and, most likely, all polymers with weak intermolecular forces) at elevated temperatures is governed by trapped entanglements. In turn, deformation studies, technologically important in themselves, offer a simple means to investigate in detail the process of entanglement trapping, a focal point in the crystallization of flexible polymers. Neutron scattering produces information on the overall dimensions of macromolecules but fails to furnish knowledge of chain intertwinings and entanglements. The latter features are by far more important than the crystalline details, since they determine the intercrystalline coherence and therefore largely the macroscopic mechanical properties of polymeric materials.

We have addressed the problem of chain *dis*entangling and how remarkably sensitive it is reflected in the deformation behavior. The inverse process, i.e., *re*entangling of disentangled solution-crystallized macromolecules through storage above the melting temperature, can conveniently be studied in a similar way.[1a] Such a study should yield a wealth of information about macromolecular motion.

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