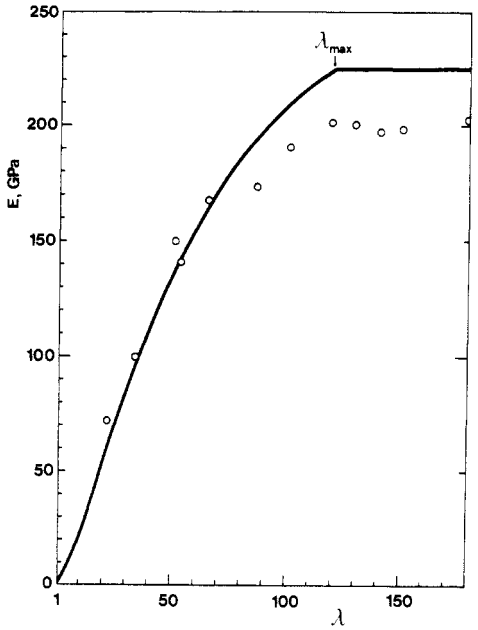

Figure 2. Young's modulus of gel-spun/drawn polyethylene ($\bar{M}_w = 2 \times 10^6$) filaments taken from ref 15. Solid line calculated according to eq 10 with $E_0 = 1.6$ GPa and $E_h = 300$ GPa. "Cutoff" at $\lambda = 120$ corresponds to maximum draw ratio for polyethylene of molecular weight 2×10^6 (see text).

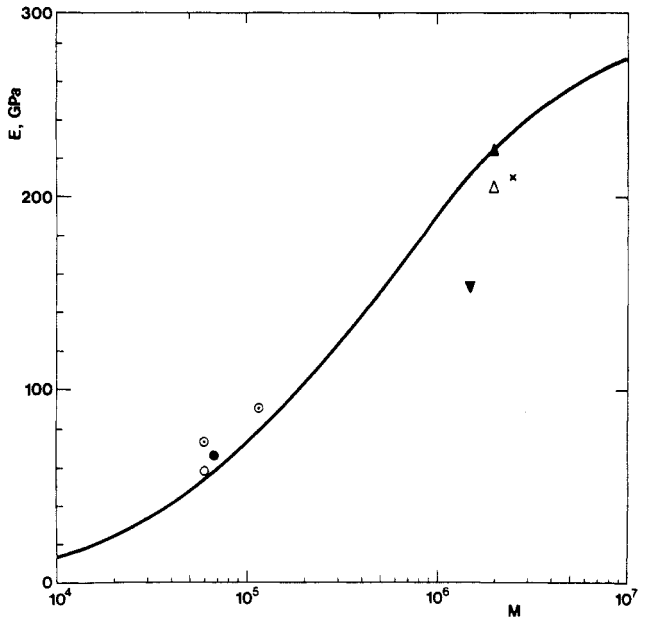

Figure 3. Predicted maximum axial Young's modulus achieavable through tensile drawing as function of molecular weight, calculated for polyethylene with eq 1 and 10. Also plotted are the reported maximum moduli for samples of various molecular weights: (●) ref 5; (○) ref 16; (△) ref 14; (⊙) Wu, W.; Black, W. B. *Polym. Eng. Sci.* **1979**, *19*, 1163. (▲) Kanamoto, T. Tsuruta, A.; Tanaka, K.; Takeda, M.; Porter, R. S. *Polym. J. (Tokyo)* **1983**, *15*, 327; (×) Kavesh, S.; Prevorsek, D. C. U. S. Patent 4 413 110, 1983; (▼) Barham, P. J.; Keller, A. *J. Mater. Sci.* **1980**, *15*, 2229.

recoiling occur, resulting in reduced efficiency of the drawing process. This is manifest experimentally as a decreasing slope of the modulus/draw ratio curve with increasing draw temperature.[16-18] Under such experimental conditions the affine approximation clearly is no longer valid, and the predicted moduli are inevitably too high.

The calculation of the modulus acknowledged only two types of elastic elements, i.e., helix and coil, which obviously is an oversimplified description of the actual structure of drawn polymers. We consider this, however, to be one of the major merits of the presented treatment. In contrast to our theory, other models[19-21] assume a more detailed fiber morphology, characterized typically by a number of structural parameters. These parameters, often not readily accessible, must be determined before computation of the modulus is possible. The "aggregate" model of Ward and co-workers[9] from which the present mechanical model is essentially derived, is, according to the authors, of limited applicability "because of the complex changes in morphology and molecular mobility which occur on drawing". It would appear from our work that these complex changes underlying the development of the modulus with draw ratio are adequately reflected in a simple helix-coil representation.

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Theory of the Helix-Coil Transition in Singly Cross-Linked, Two-Chain Coiled Coils. 2. Role of Mismatched States

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Table I
Comparison of the Helix Content in the Subpopulation of Singly Cross-Linked, Homopolymeric, Coiled Coils Containing at Least One Pair of Interacting α-Helical Turns Calculated in the Loops-Excluded, $f_d°$, and the Imperfect Matching Interior Eyelet, f_d, Models as a Function of Helix–Helix Interaction Parameter[a]

w	$f_d°$ [b]	f_d [c]	w	$f_d°$ [b]	f_d [c]
1.0	0.361 467 20	0.361 454 99	2.0	0.388 592 94	0.388 587 11
1.1	0.362 784 74	0.362 773 43	2.1	0.396 523 94	0.396 518 49
1.2	0.364 225 61	0.364 215 14	2.2	0.408 213 97	0.408 208 84
1.3	0.365 823 11	0.365 813 40	2.3	0.427 215 74	0.427 210 84
1.4	0.367 621 04	0.367 612 04	2.4	0.462 344 68	0.462 339 87
1.5	0.369 678 53	0.369 670 17	2.5	0.533 060 55	0.533 055 58
1.6	0.372 077 63	0.372 069 87	2.6	0.653 274 82	0.653 269 49
1.7	0.374 936 03	0.374 928 82	2.7	0.776 662 75	0.776 657 37
1.8	0.378 429 07	0.378 422 36	2.8	0.852 908 90	0.852 903 92
1.9	0.382 830 45	0.382 824 21	2.9	0.891 924 03	0.891 919 60
			3.0	0.913 084 47	0.913 080 58

[a] $N_B = 71$, $N_C = 3$, $\sigma = 10^{-2}$, $s = 0.94$, $m = 4$, $m_l = 2$, $m_r = 3$, $l_c = 2$, $r_\phi = 10^{-1}$, and $u_\phi = 359$ Å^3. (See text and ref 1 for definition of symbols.) The differences in $f_d°$ and f_d are italic. [b] Calculated via eq II-8a ff of ref 1. [c] Calculated via eq II-11a ff of Supplementary Material.

part of an effort to understand the role of topological constraints in the conformational transitions of model protein systems, we developed two models of the helix–coil transition in singly cross-linked, two-chain, coiled coils.[1] Recognizing the prohibitive entropic cost of forming constrained random coil loops, we formulated the "loops-excluded" model (LEM), which ignores the presence of such topologically constrained states and leads to the requirement that either the pair of α-helical turns (blocks) containing the cross-link is fully helical and interacting or there are no interacting α-helices present in the molecule. The second, in principle far less restrictive, "interior eyelet" model (IEM) included, in addition to those states of the LEM, constrained random coil loops originating at the cross-link and ending on a pair of interacting α-helices. In paper 1, the IEM was artificially restricted to include only in-register, interacting α-helical states; i.e., helical block i in chain 1 can only interact with helical block i in chain 2. In the perfect matching limit, the LEM and IEM give essentially identical results. Otherwise stated, due to net effect of loop entropy, constrained interior random coiled loops can be safely ignored. We further conjectured that even if out-of-register states are included, the IEM and the LEM should be equivalent. In this Note we summarize results of the extension of the IEM to include such out-of-register states in the imperfect matching interior eyelet model (IMIEM) and demonstrate the validity of the above conjecture. As the basic methodology has been developed elsewhere,[1,2] we relegate details of the formalism to the Supplementary Material.

Since the IMIEM permits randomly coiled, cross-linked blocks in molecules containing interacting helices and the LEM does not, the helix content of the subpopulation of molecules containing at a minimum a single pair of interacting helices and calculated in the IMIEM, f_d, is always less than or equal to $f_d°$, the helix content of the same subpopulation calculated via the LEM. Moreover, for all values of the helix–helix interaction parameter w, it is the agreement of f_d with $f_d°$ that determines the range of validity of the loops-excluded model. (Both models give the same value for the helix content of the noninteracting configurations of the two chains.)

In the calculations discussed below, we have set the number of residues per block, m, equal to 4, the number of residues to the left (right) of and including the cross-link equal to 2 (3) and the Zimm–Bragg helix propagation parameter[3] $s = 0.94$, and assume a uniform, site-independent w. The effective bond length of the cross-link is assumed to be equal to that of two amino acid residues.

For the entire range of σ, number of blocks N_B, and cross-linked block location N_C studied, we found that f_d and $f_d°$ agree to at least four significant figures throughout the entire course of the helix–coil transition. In the representative table discussed below, the differences in the values of $f_d°$ and f_d are in italics. In Table I, we set $\sigma = 10^{-2}$, $N_B = 71$, and $N_C = 3$, thereby emphasizing the importance of constrained random coil loops originating at the cross-link. Thus, on the basis of Table I and additional calculations not shown we conclude that *mismatched states* in *singly cross-linked molecules* are completely *unimportant*.

The present work has implications for the non-cross-linked molecules as well. We have established that independent of cross-link location, there are no mismatched, interacting helical states in singly cross-linked molecules. Moreover, it is straightforward to show that the helix content of a non-cross-linked molecule containing interacting helices is in fact related to an average of f_d summed over all cross-link locations. Thus, in non-cross-linked chains our original conjectures that interacting molecules contain a single interacting helical stretch[4,5] and that the only mismatched, interacting helical states are those that are out-of-register are confirmed.[2]

The result that mismatched states and constrained interior random coil loops originating at the cross-link can be ignored points out once again the dominant role played by loop entropy in determining the character of the helix–coil transition in coiled coils. In non-cross-linked chains of moderate length, as mentioned above, loop entropy restricts the number of interacting helical stretches in a given molecule to one, but out-of-register, interacting helices are allowed. The interacting helical stretch may occur any place in the molecule and be of arbitrary length. The introduction of a single cross-link has greatly restricted the available phase space. Mismatched interacting helical conformations are now essentially irrelevant and either the single, interacting helical stretch includes the cross-link or the molecule does not have any interacting pairs of helices. In essence, we have a two-state model based on the conformation of the cross-linked blocks. The helix–coil transition is still continuous, but the conformational transition is more cooperative. It is of further interest what happens when a second cross-link is introduced; this situation will be examined in a forthcoming paper.[6]

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Supplementary Material Available: Formal theory of the helix–coil transition in singly cross-linked, two-chain, coiled coils—role of mismatched states (15 pages). Ordering information is given on any current masthead page.

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