

Meander Model of Amorphous Polymers Morphology, Rubberelasticity, Rheology

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Summary

The present state of the meander model is reviewed and a detailed derivation of the magnetic birefringence is given within this frame.

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Introduction To develop a most realistic molecular model of amorphous polymers, polymer melts or concentrated solutions, there are essentially two conceptual ways of approach: (a) from the isolated coil in dilute solution or (b) from the extended chain polymer crystal.

The first approach is well known (FLORY 1953,1969; DE GENNES 1979) - using the assumption of interpenetrating coils, obviously conserving most of their entropy - and e.g. accounts of the rubberelasticity of uncross-linked polymer melts by the action of chain entanglements. But a more detailed description (e.g. of chain deformation and intermolecular interactions, favouring at least partial chain parallelism (VEH 1979)) is difficult to achieve on a molecular scale.

In the second approach (PECHHOLD et al. 1979, 1979a, 1980, 1982) one starts at a well defined state of similar density and proceeds stepwise by introducing definite types of disorder (based on potential calculations) that must quantitatively account for the observed structural and mobility changes. In the statistical mechanics of disorder the cluster-entropy-hypothesis (CEH) is used throughout, and states:

Clustering in subspace (e.g. conformation, dislocation, orientation, deformation) of m equivalent elements (e.g. segments, s -dislocations, s -lines, s -layers), each having f accessible states (vibrational, conformational states, etc.), does not reduce entropy as long as $m < f$.*

Whereas perfect polymer crystals consist of parallel chains of only one low energy conformation, high temperature phases exist (e.g. in PE and t-1, 4-PBD) that have accumulated more than half of the entropy of melting, but which still appear crystalline. Thermodynamic data of these conformational transitions are explained by assuming a mixture of energetically favoured chain conformations, realized in conformational clusters. The subsequent melting can be accounted for by cooperatively formed dislocation walls, the statistical element being the segment-dislocation (number of segments in a line between walls). This short range order concept of the melt applies quite as well to amorphous atactic polymers and favours chain parallelism across longer distances, because mutual penetration of neighbouring chains should increase energy more than gain entropy.

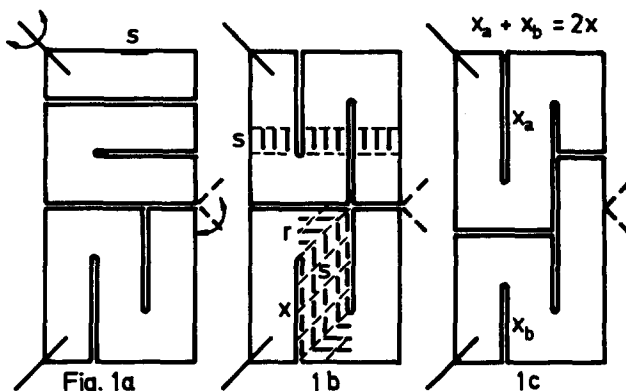
With regard to the overall geometry of a macromolecule within a nearly parallel chain arrangement, the melt bundle is introduced, in which statistical tightfolding and reptation of each molecule results in a one dimensional coil appearance.

* For low molecular systems, CEH has so far been applied in a dislocation theory of melting, a vacancy theory of evaporation and a cube-model theory of liquid crystals.

The meander model If one adopts this bundle concept (which has been already proposed by KARGIN in 1957), two main questions have to be answered: (i) how large is the diameter, r , of the bundle and (ii) how far does it extend in one direction. Both problems can be solved simultaneously by using equilibrium statistics and essentially CEH. The basic idea is that chain segments gain orientational entropy if the bundle changes its direction by sharply bending and/or superfolding.

The most simple and symmetric topology in which a melt bundle can tightly superfold, densely to fill 3-dimensional coarse grains (for the bulk phase) or plane grains (for thin surface films), is an arrangement of meander cubes (PECHHOLD et al. 1979, 1980, 1982)[†]. To enable these cubes to occupy all 3 accessible sites, the meandering bundle is assumed to link them via their cube diagonals serving as axis of rotational diffusion (fig.1a). For the quantitative treatment of the proposed superstructure statistical elements must be defined (fig.1b) which are adapted to control

- (i) superfolding: segment-line of a bundle, containing r/d segments of length s .
- (ii) cube rotation: segment-line across the meander cube, consisting of $(r+x)/d$ segments.
- (iii) shear deformation: molecule layers of the cube, composed of $(r+x)^2/s \cdot d$ segments.



Meander topology and definition of statistical elements

The excess free energy Δg_s per segment due to these orientational and deformational states of the bundle becomes (PECHHOLD et al. 1979, 1980, 1982)

(superfolding per half meander layer)	(cube rotation)	(shear deformation)
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$$[1] \quad \frac{\Delta g_s}{kT} = \frac{d}{r} \frac{s}{r+x} \left[\frac{\Delta g_f^*}{kT} + \frac{r}{d} \frac{\Delta g_k}{kT} - \ln \frac{\frac{r+x}{s}!}{\frac{x}{s}! \frac{r}{s}!} \right] + \frac{d}{r+x} \frac{\Delta g_{rot}}{kT} + \frac{d \cdot s}{(r+x)^2} \frac{\Delta g_{def}}{kT}$$

free energy of formation of one superfold
formation of $2r/d$ chain-bends
orientational entropy of s -line clusters which differ in chain direction

According to immobilization effects Δg_f^* will be approximately proportional to T (PECHHOLD, GROSSMANN 1979). The contributions Δg_{rot} and Δg_{def} have been discussed in (PECHHOLD et al. 1979, 1980): $\ln 3 > (-\Delta g_{rot}/kT) > 0.13$, depending on temperature and on the kind of the polymer; $(-\Delta g_{def}^{rot}/kT) \approx 3 \ln 2 + \ln(3r/d)$, will be taken as constant here.

To get the equilibrium values of x/r and r/s , a preliminary minimization of [1] is performed (PECHHOLD et al. 1982), showing that the total minimum of Δg_s is in the range $1.5 < x/r < 2.5$ for reasonable $\Delta g_f^*/kT$ -data. Therefore

[†] 3-dimensional drawings of the meander topology are reproduced in (PECHHOLD et al. 1979, 1979a, 1980, 1982).

it is justified to use $x/r=2$ (and not 4,6,...) as geometrical condition from cubic topology. Repeating the minimization for r/s (at fixed $x/r=2$), the equilibrium meander superstructure can be characterized by

$$[2] \quad \frac{x}{r} = 2, \quad [3] \quad \frac{r}{d} \approx \frac{s}{d} \frac{\Delta g_f^*}{kT}, \quad [4] \quad \left. \frac{\Delta g_s}{kT} \right|_{eq} \approx -\frac{d}{3r}$$

The formulas [3,4] are approximations, but should deviate no more than 20% from the more complete results (PECHHOLD et al. 1982). Fluctuations in x/r and r/s have to be allowed but must not violate topology. Relying on CEH these fluctuations can be described by reversibly coupling of any two adjacent cubes in suitable relative orientation (x/r -fluctuation, fig.1c) and by changing the contour of the bundle cross-section without varying its area (r/s -fluctuation).

At medium and even more at lower chain molecular weights the bundle diameter r decreases, because pairs of chain ends will be substituted for the tight chain folds within the superfolds, thereby reducing Δg_f^* - in the idealized geometrical case - to $\Delta g_f^* \approx \Delta g_{f\infty}^* (1-w)$; $w=r(r+x)/L \cdot d$ being the geometrical probability to find a pair of chain ends within a half meander layer. From [3] one therefore approximately gets

$$[5] \quad \frac{r}{r_\infty} = \frac{A}{2} \left[\left(1 + \frac{4}{A}\right)^{1/2} - 1 \right], \quad \text{with } A = \frac{L \cdot d}{3r_\infty^2}, \quad L \text{ extended chain length, } d \text{ average chain distance}$$

In fig.2 (taken from (PECHHOLD, GROSSMANN, 1979) $3r(M)$ is plotted for PE and PS, using the most probable r_∞ values. The approximate validity of [5] has been shown for polyisobutylene from shear compliance analysis (PECHHOLD et al. 1979a). Further checks are in progress. Fig.2 also contains the radius of gyration $R_g(M)$ of completely labelled chains in the cube meander topology, together with some SANS-data from various

authors. p_f is the probability for tight folds in the molecule.

There are several experimental results from which the

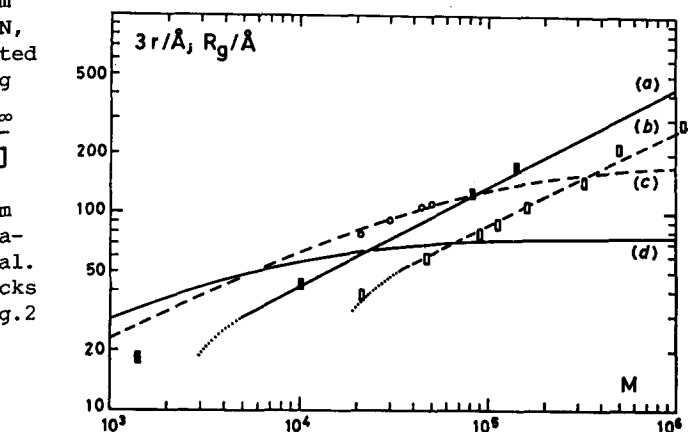


Fig. 2 Molecular weight dependence of the meander size $3r$ and the radius of gyration R_g for PE- and PS-melt. (a) R_g^{PE} , (b) R_g^{PS} , (c) $3r^{PS}$, (d) $3r^{PE}$

$$R_g^2 \approx \frac{1}{6}(3r)^2 + \frac{l^2 M}{81.2 M_l p_f} \left\{ 1 - \frac{3}{2np_f} \left[1 - \frac{2}{2np_f} \left(1 - \frac{1}{2np_f} \right) \right] \right\}$$

	M_l	$l/\text{Å}$	$d/\text{Å}$	$r_\infty/\text{Å}$	$-RT \ln p_f / \text{kJ mol}^{-1}$
PS	52	1.2	8.7	60	20
PE	14	1.2	4.8	25	18

meander cube side length $3r/d$ (measured in lateral chain distances) can be evaluated if the analysis is carried out in the frame of the meander model (essentially using CEH). The $3r/d$ -methods which have so far been applied - some extensively, some in the very beginning - are listed in the following, together with references and relevant formulae.

meander theory (PECHHOLD et al. 1979, 1980, 1982) and semi-empirical potential calculations

$$[3] \quad \frac{r}{d} \approx \frac{s}{d} \frac{\Delta g_f^*}{kT}$$

plateau-compliance J_{eN}^0 (PECHHOLD et al. 1979a, 1980) (rubberelasticity)

$$[6] \quad J_{eN}^0 = \frac{1}{9} \frac{d^3}{kT} \left(\frac{3r}{d} \right)^2$$

glass relaxation by freezing out segment-dislocations (PECHHOLD et al. 1979a) (activation diagram analysis)

$$[7] \quad f_{max} = \frac{v_0}{\pi} e^{-\frac{Q_g}{kT}} \left[1 - \left(1 - e^{-\frac{\epsilon_s}{kT} \frac{3r}{d}} \right)^2 \right]$$

ratio of relaxation frequencies (PECHHOLD et al. 1979a)

$$[8] \quad \frac{f_{max}^G}{f_{max}^J} \approx (3r/d)^4$$

anomalous superheating effect at melting (PECHHOLD et al. 1982)

$$[9] \quad \frac{\Delta T_m}{T_m^\infty} \approx -\frac{d}{3r} \frac{kT_m^\infty}{\delta h_s}$$

magnetic birefringence

$$[20] \quad \Delta n = \frac{4\pi}{15} \frac{3r}{d} \frac{N}{V} \frac{n^2+2}{3n} \left(\frac{3r-1}{2} \right)^2 P_2^2(\theta) \Delta \chi^m \Delta \alpha^m \frac{B^2/k}{T-T_u}$$

oligomer/polymermixtures (PECHHOLD et al. 1982)

radius of gyration of a few percent of oligomer reflects the superstructure of the environment (SANS in n-alkanes/d-PE and oligostyrenes/d-PS)

Langmuir-gauge

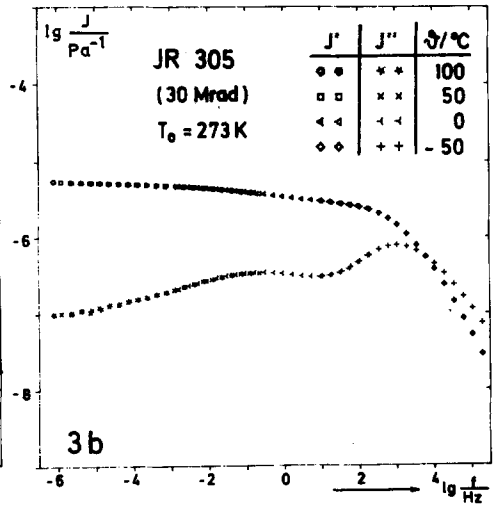
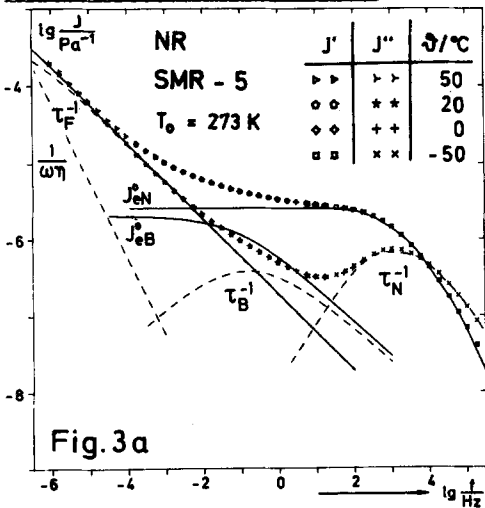
polymers with only slight spreading tendency form thin films of thickness 3r or twice of it

electronmicroscopy (PECHHOLD et al. 1982)

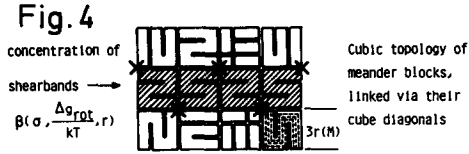
surface overgrowth, thin film thickness and structure

Because the results of orientation correlation methods, like magnetic birefringence, were interpreted as to disproof the meander model, a detailed derivation of [20] is given in the appendix and a comparison with experimental data added. For some polymers (PE, PS, PIB, NR) almost all above methods have been applied and result - within experimental accuracy - in well matched 3r/d-values. For most polymers the high molecular weight limit $3r_\infty/d$ is in the range 15 - 30.

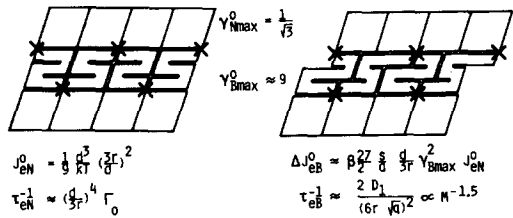
Rubberelasticity and rheology



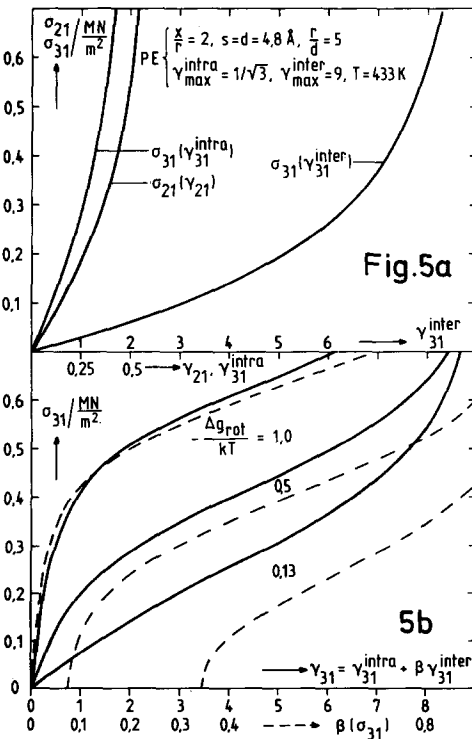
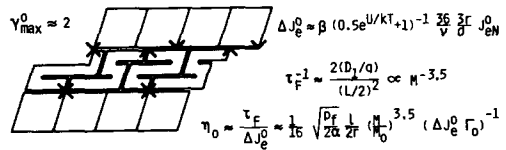
In the meander model, rubber-elasticity needs a more complex interpretation (PECHHOLD et al. 1979, 1980, 1981) than in the coil model. Fig.3 shows complex compliance master curves for cis-Polyisoprene in the uncrosslinked (a) and 30-Mrad crosslinked (b) state. They can be decomposed at least into 3 (a) and 2 (b) relaxation processes, the low frequency flow relaxation being absent in the crosslinked sample: The coupled meander cubes within a coarse grain perform shear fluctuations, restricted to one chain distance per layer of molecules (intra meander shear, mediated by dislocation movement, fig.4). This topological restriction compares with that of entanglements in the coil model. A deformation free energy consideration leads to the plateau-compliance J_{eN} . This



Deformation modes, its compliances ΔJ and relaxation rates $\tau^{-1}(\sigma \rightarrow 0)$



Flow-relaxation and viscous flow (of fractions)



deformation mode can account for only $\gamma_{max}^{intra} \approx 0.58$ (fig.5a, steep curves). Beyond these intra meander shear fluctuations large scale deformations become possible by interbundle displacements, i.e. by unfolding of suitable arranged meander cubes (fig.4). To this purpose whole files of meander cubes or even layers of them must cooperate in a shearband process, the stress-strain behaviour of which is shown in fig.5a ($\gamma_{max}^{inter} \approx 9$). In the statistical deformation theory (PECHHOLD 1980) this characteristic of an already developed shearband, the stress-dependent concentration β of shearbands (fig.5b, dashed curves) and the superposition of intra- and interbundle shear (fig.5b, full curves) have been derived. From this molecular theory the nonlinear characteristic of any type deformation (e.g. uniaxial, PECHHOLD 1980) can be evaluated, if the meander size $3r/d$ and the rotational free energy $\Delta g_{rot}/kT$ are known for a given polymer.

Fig.5 Theoretical stress-strain behaviour in shear for high molecular PE-melt.

Magnetic birefringence Assuming an anisotropic molar susceptibility ($\chi_{3,3}^m, \chi_{1,1}^m = \chi_{2,2}^m$) of the monomer, the 3'-axis of which is tilted against the main chain axis 3 by an angle θ , the susceptibility of a chain segment of generally two monomers becomes

$$[10] \quad \chi_{33}^s = 2\chi_{1,1}^m \sin^2\theta + 2\chi_{3,3}^m \cos^2\theta, \quad \chi_{11}^s = (\chi_{3,3}^m - \chi_{1,1}^m) \sin^2\theta + 2\chi_{1,1}^m$$

The superstructural unit (e.g. a straight chain cube or the meander cube) may contain a fraction ζ of chain segments oriented parallel to the 3-axis and $(1 - \zeta)$ segments perpendicular to it (e.g. $\zeta = 1$ or $\zeta = 2/3$). Then its segmental susceptibility may be written

$$[11] \quad \chi_{33}^u = \zeta\chi_{33}^s + (1-\zeta)\chi_{11}^s, \quad \chi_{11}^u = \frac{1}{2}(1-\zeta)\chi_{33}^s + \frac{1}{2}(1+\zeta)\chi_{11}^s$$

A coarse grain of cubic units may now be composed of z such cubes and $(1-z)$, rotated (around the space diagonal) to the other two position. Then the susceptibility per segment of this oriented grain becomes (after some calculation)

$$\begin{aligned} \chi_{33}^g &= \frac{2}{3} \frac{3z-1}{2} \frac{3\zeta-1}{2} (\chi_{33}^s - \chi_{11}^s) + \frac{1}{3} (\chi_{33}^s + 2\chi_{11}^s) \\ &= \frac{4}{3} \frac{3z-1}{2} \frac{3\zeta-1}{2} P_2(\theta) (\chi_{3,3}^m - \chi_{1,1}^m) + \frac{2}{3} (\chi_{3,3}^m + 2\chi_{1,1}^m) \\ [12] \quad \chi_{11}^g &= -\frac{1}{3} \frac{3z-1}{2} \frac{3\zeta-1}{2} (\chi_{33}^s - \chi_{11}^s) + \frac{1}{3} (\chi_{33}^s + 2\chi_{11}^s) \\ &= -\frac{2}{3} \frac{3z-1}{2} \frac{3\zeta-1}{2} P_2(\theta) (\chi_{3,3}^m - \chi_{1,1}^m) + \frac{2}{3} (\chi_{3,3}^m + 2\chi_{1,1}^m) \end{aligned}$$

If a magnetic field B is applied along a 3''-axis, related to the 3-axis of the cubic superstructure within the grain by a tilt angle ψ , the respective susceptibilities per segment in the 3''- and 1''-directions read

$$\begin{aligned} \chi_{3''3''}^g(\psi) &= \frac{4}{3} \\ [13] \quad &\left\{ \frac{3z-1}{2} \frac{3\zeta-1}{2} P_2(\theta) P_2(\psi) (\chi_{3,3}^m - \chi_{1,1}^m) \right\} + \frac{2}{3} (\chi_{3,3}^m + 2\chi_{1,1}^m) \\ \chi_{1''1''}^g(\psi) &= -\frac{2}{3} \end{aligned}$$

In that field B the diamagnetic energy ϵ of a segment line (of $3r/d$ segments, which is the statistical element for meander cube rotation) becomes

$$[14] \quad \epsilon = \frac{1}{2} \frac{3r}{d} \chi_{3''3''}^g(\psi) B^2$$

To calculate the orientational order parameter $z = (1+\eta)/2$ of a grain at fixed angle ψ and in internal equilibrium, one has to introduce ϵ into the segment line free energy of cube rotation Δg_{rot} (cf. PECHHOLD 1980, equation [6a], or PECHHOLD, GROSSMANN 1979 [9.2]) and to solve the minimization equation (PECHHOLD 1980 [8a] or PECHHOLD, GROSSMANN 1979 [5.4]) -which now contains an additional term $\frac{1}{2} \frac{3r}{d} [\partial \chi_{3''3''}^g(\psi) / \partial z] B^2 / kT$ on the left hand side - for η . This can be performed by expanding η around its equilibrium value $(-1/3)$ in the isotropic state, i.e. for $T > T_u$

$$[15] \quad \eta \approx -\frac{1}{3} - \xi, \quad \text{with } \xi(B) \ll 1$$

After some calculations, one gets the intermediate relations

$$\frac{1-\eta}{1+\eta} \approx 2 \left(1 + \frac{9}{4} \xi\right), \quad \alpha \approx \frac{1}{3} \frac{2+E}{E} - \frac{1}{2} \xi \frac{1+E-2E^2}{E(2+E)} \quad \text{and}$$

$$\frac{\alpha+\eta}{\alpha-\eta} \approx \frac{1}{1+E} \left[1 - \frac{27}{4} \frac{E}{2+E} \xi\right], \quad \text{with } E = \exp(-g/kT) \quad \text{as in (PECHHOLD et al. 1979, 1980)}$$

and finally the solution of the equilibrium condition (PECHHOLD 1980 [8a] or PECHHOLD, GROSSMANN 1979 [5.4])

$$[16] \quad \frac{3z-1}{2} = \frac{3\eta+1}{4} \approx \frac{3}{4} \xi \approx \frac{1}{6} \frac{3r}{d} \left[\partial \chi_{3''3''}^g(\mathfrak{D}) / \partial z \right] \frac{B^2}{kT} \frac{2+E}{7E-4}$$

The last factor on the right side is equal to 1 for $T \rightarrow \infty$ and becomes ≈ 23 for $T=T_u$, because $E = \sqrt[4]{4-1}$. It can be approximately written as $T/(T-T_u)$, but one should keep in mind that it really diverges a little below T_u (which is an interesting finding with regard to the susceptibility behaviour near phase transitions).

The magnetic birefringence $\Delta n \ll n$, of a \mathfrak{D} -oriented grain, is related to the anisotropic polarizability via Clausius-Mossotti's formula

$$[17] \quad \Delta n(\mathfrak{D}) = 2\pi \frac{N}{V} \frac{n^2+2}{3n} \left[\alpha_{3''3''}^g(\mathfrak{D}) - \alpha_{1''1''}^g(\mathfrak{D}) \right]$$

in which N/V is the number of chain segments per unit volume, and the difference in polarizabilities can be reduced to the monomeric anisotropy using [13] respectively

$$[18] \quad \Delta n(\mathfrak{D}) = 4\pi \frac{N}{V} \frac{n^2+2}{3n} \frac{3z-1}{2} \frac{3\zeta-1}{2} P_2(\theta) P_2(\mathfrak{D}) (\alpha_{3',3'}^m, -\alpha_{1',1'}^m)$$

Introducing (3z-1) from [16] and carrying out the differentiation, one gets for the magnetic birefringence of a \mathfrak{D} -oriented grain - using the abbreviations $\Delta\alpha^m = \alpha_{3',3'}^m - \alpha_{1',1'}^m$, $\Delta\chi^m = \chi_{3',3'}^m - \chi_{1',1'}^m$,

$$[19] \quad \Delta n(\mathfrak{D}) \approx \frac{4\pi}{3} \frac{3r}{d} \frac{N}{V} \frac{n^2+2}{3n} \left(\frac{3\zeta-1}{2}\right)^2 P_2^2(\theta) P_2^2(\mathfrak{D}) \Delta\chi^m \Delta\alpha^m \frac{B^2/k}{T-T_u}$$

which finally becomes after spatial averaging over \mathfrak{D}

$$[20] \quad \Delta n \approx \frac{4\pi}{15} \frac{3r}{d} \frac{N}{V} \frac{n^2+2}{3n} \left(\frac{3\zeta-1}{2}\right)^2 P_2^2(\theta) \Delta\chi^m \Delta\alpha^m \frac{B^2/k}{T-T_u}$$

Comparing the theoretical result [20] with experimental data of Δn or the Cotton-Mouton constant $C_m = \Delta n / \lambda B^2$, determined for some polymers by STAMM 1977, one can evaluate $3r/d$, provided that the monomeric $\Delta\chi^m$ and $\Delta\alpha^m$ are known. Using the findings $\Delta n \approx 4.1 \cdot 10^{-9} B^2$ ($[B] = 1T$) and the parameters for polystyrene (PS), given in (STAMM 1977): $\rho = 1.05 \text{ g cm}^{-3}$, $M_S = 2 \cdot 10^4 \text{ g/mol}$, $N/V = N_A \rho / M_S \approx 3.0 \cdot 10^{21} \text{ cm}^{-3}$, $n = 1.6$, $\Delta\chi^m \approx 5 \cdot 10^{-4} \text{ JT}^{-2} \text{ mol}^{-1}$, $\Delta\alpha^m \approx 6.0 \cdot 10^{-24} \text{ cm}^3$, $T - T_u \approx 373 \text{ K}$, and $\theta \approx 20^\circ$ (from semiempirical potential calculations (BECK 1976) of quasiplanar (t \bar{g} t \bar{g}) SPS- and IPS-helices), one finds from [20] (with $\zeta = 2/3$), that the relative meander cube side length $3r/d \approx 10.5$, which fits the prediction (cf. PECHHOLD 1980, fig.13 or PECHHOLD, GROSSMANN, fig.6) for a $M \approx 30.000PS$, used by STAMM 1977.

In a paper by FISCHER et al. 1976, fig.4, Δn -data on the PS dimer and short chain oligomers are reported, which are smaller by roughly a factor 1.6 than those on PS. Choosing a single segment as the statistical element (in contrary to $3r/d$ segments for the meander cube) and assuming a straight packing of elements into small cubic units ($\zeta = 1$) and also $\theta \approx 0^\circ$ one gets from [20] (with all other parameters unchanged) a Δn which is smaller by a factor 1.7 compared with that of PS.

For poly-N-vinylcarbazol (PVCA, $M_w \approx 410000$) STAMM 1977 got $C_m \approx 60 \cdot 10^{-5} T^{-2} \text{ cm}^{-1}$ from extrapolation of measurements on $< 10\%$ PVCA-chloroform solutions at 20 to 65°C. Comparing this with $C_m \approx 6.5 \cdot 10^{-5} T^{-2} \text{ cm}^{-1}$ for polystyrene at 373 K one finds, for PVCA $\Delta n \approx 30 \cdot 10^{-9} B^2$. Using the parameters $\rho = 1.19 \text{ g/cm}^3$, $M = 2 \cdot 193 \text{ g mol}^{-1}$, $N/V = 1.85 \cdot 10^{21} \text{ cm}^{-3}$, $n = 1.7$, $\Delta \chi^m \approx 2 \cdot \Delta \chi^m(\text{PS}) \approx 10 \cdot 10^{-4} \text{ JT}^{-2} \text{ mol}^{-1}$, $\Delta \alpha^m = 2 \cdot \Delta \alpha^m(\text{PS}) \approx 12 \cdot 10^{-24} \text{ cm}^3$, $T - T_u \approx 373$, $\theta \approx 20^\circ$ as in PS, [20] yields the meander cube side length $3r/d \approx 30$. This value is not unreasonable because of the high molecular weight, but will still be reduced to 20, if θ should approach 0° .

Finally, [20] shall be applied to a liquid crystal, MBBA, in its isotropic phase. The magnetic birefringence was shown (STINSON, LITSTER 1970) to follow $\Delta n/B^2 \approx 2.2 \cdot 10^{-6} \cdot (T - T_u)^{-1}$. Taking $\Delta \chi(\text{molecule}) = 2 \cdot \Delta \chi^m \approx 5 \cdot 10^{-4} \text{ JT}^{-2} \text{ mol}^{-1}$, and the normal birefringence, $n_{||} - n_{\perp} \approx 2\pi \frac{N}{V} \frac{3n}{n^2 + 2} \Delta \alpha^m \approx 0.25$ (KELKER, HATZ 1980), both from an extrapolation to the completely oriented nematic state, the formula [20] yields $\Delta n/B^2 \approx 2.1 \cdot 10^{-6} (T - T_u)^{-1}$, taking into account that $\zeta = 1$ and $\theta = 90^\circ$.

These examples show that, on the basis of CEH, orientation correlations of oligomers and polymers - as described in those cube models - do not at all contradict the experimental data (as has been stated e.g. in (FISCHER et al. 1976)).

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