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Chain Thickness and Polymer Conformation in the Crystalline State

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ABSTRACT: Empirical equations relating polymer cross-sectional area A and molecular mass per main-chain bond m_0 are derived for linear, flexible chain polymers with either extended or helical conformation in the crystalline state, and relevance of the results obtained to some of the earlier correlations is briefly discussed.

In a recent series of papers Boyer and Miller[2-6] have found that "thickness" of a macromolecule, a (or, equivalently, its cross-sectional area, $A = a^2$), is a useful empirical parameter correlated with various physical properties of linear, flexible-chain polymers. It is the purpose of the present note to develop a simple method for quantitative estimation of this parameter from chemical structure of the chain repeating unit. Preliminary results were published earlier.[7]

We start from the observation that A is related to the crystalline molar volume, V_c, as $V_c = Ad$, where d is the identity period. On the other hand, $V_c = v_cM/N_A$, where v_c is the crystalline specific volume, M is the molecular mass of the repeating unit, and N_A is the Avogadro number. Combining the above expressions, one obtains

$$A = v_cM/dN_A = m_0v_c/d_0N_A \qquad (1)$$

where $m_0 = M/n$, $d_0 = d/n$, and n is the number of main-chain bonds in the chain repeating unit. Since d_0 depends primarily on the chain conformation in the crystalline state, and v_c varies in a relatively narrow range, at least for polymers with essentially similar chemical composition, it follows that A should correlate with the molecular mass per main-chain bond, m_0. This conclusion is not inconsistent with Bondi's tabulations[8] from which it becomes apparent that the van der Waals radii of elements within a specific family (e.g., halogens) tend to increase with their masses.

Values of A for a large number of flexible-chain polymers[9] listed in Table I are plotted in the double-logarithmic coordinates against m_0 in Figure 1. As already observed on several occasions,[10-12] the resulting plots split into three straight lines for polymer series differing in their crystalline conformations. Thus, the lowest slope is observed for polymers with essentially extended chain conformations (EC polymers) in the crystal (line A in Figure 1), while considerably higher slope attends the line B for vinyl polymers crystallizing in helical conformations 3/1, 7/2 and the like (HC_1 polymers). Line C for polymers with bulky and/or long side substituents which have looser helical conformations 11/3 or 4/1 in the crystalline state (HC_2 polymers) is shifted upward approximately parallel to line B. The observed dependences are adequately (average correlation coefficients above 0.92) described by the following empirical equations for the EC, HC_1, and HC_2 polymer series, respectively.[7,9]

$$A\ (\text{Å}^2) = 4.65m_0^{0.5} \qquad (2a)$$

$$A\ (\text{Å}^2) \simeq 1.41m_0 \qquad (2b)$$

$$A\ (\text{Å}^2) \simeq 2.05m_0 \qquad (2c)$$

As discussed in more detail elsewhere,[10] dramatic dependence of A on polymer chain conformation in the crystalline state can be traced back to conformation dependence of d_0 and (intramolecular) packing coefficient.[13]

Table I
Chain Cross-Sectional Areas for Different Polymer Series

no.	chain repeating unit	M	n	A, Å^2	helix
1	butene-1 (form 1)	56.10	2	45.22	3/1
2	butene-1 (form 2)	56.10	2	55.28	4/1
3	3-methylbutene-1	70.14	2	73.53	4/1
4	ethylene	14.03	1	18.28	1/1
5	chlorotrifluoroethylene	116.47	2	35.61	14/1
6	tetrafluoroethylene	50.01	1	27.08	13/6
7	hexadecene-1	224.43	2	237.00	4/1
8	hexene-1	84.16	2	78.68	7/2
9	4-methylhexene-1	98.19	2	97.47	7/2
10	5-methylhexene-1	98.19	2	89.85	3/1
11	isobutylene	56.10	2	41.24	8/3
12	octadecene-1	252.49	2	264.00	4/1
13	pentene-1 (form 1)	70.13	2	58.69	3/1
14	pentene-1 (form 2)	70.13	2	72.65	4/1
15	4-methylpentene-1	84.16	2	86.44	7/2
16	propylene	42.08	2	34.27	3/1
17	tetradecene-1	196.38	2	210.00	4/1
18	vinylcyclohexane	110.19	2	119.63	4/1
19	*sec*-butyl acrylate	128.17	2	92.65	3/1
20	isopropyl acrylate	114.14	2	83.30	3/1
21	*tert*-butyl acrylate	128.17	2	94.08	3/1
22	acrylonitrile	53.06	2	30.85	1/1
23	methyl methacrylate	100.12	2	63.84	5/1
24	vinyl alcohol	44.05	2	21.39	1/1
25	vinyl chloride	62.50	2	27.18	1/1
26	vinylidene bromide	185.85	2	42.22	1/1
27	vinyl fluoride	46.04	2	21.13	1/1
28	vinylidene chloride	96.95	2	35.21	1/1
29	methyl vinyl ketone	70.09	2	52.85	7/2
30	styrene	104.14	2	69.80	3/1
31	*o*-fluorostyrene	122.14	2	70.82	3/1
32	*o*-methylstyrene	118.17	2	90.35	4/1
33	*m*-methylstyrene	118.17	2	98.56	11/3
34	1-vinylnaphthalene	154.20	2	112.36	4/1
35	ϵ-caprolactam	113.16	7	17.86	1/1
36	8-aminocaprylic acid	141.21	9	18.43	1/1[a]
37	7-aminoenanthic acid	127.18	8	18.00	1/1[a]
38	11-aminoundecanoic acid	183.29	12	17.35	1/1[a]
39	hexamethylene-adipamide	226.31	14	17.60	1/1
40	hexamethylene sebacamide	282.42	18	17.82	1/1[a]
41	ethylene adipate	172.18	10	18.14	1/1
42	ethylene azelaate	214.26	13	18.51	1/1
43	ethylene sebacate	228.28	14	18.47	1/1
44	ethylene suberate	200.23	12	18.27	1/1[a]
45	ethylene succinate	144.13	8	19.46	1/1[a]
46	ethylene oxide	44.05	3	21.50	7/2
47	methylene oxide	30.03	2	17.22	9/5
48	propylene oxide	58.08	3	24.47	2/1
49	tetramethylene oxide	72.10	5	17.61	1/1

[a] Tentative assignment

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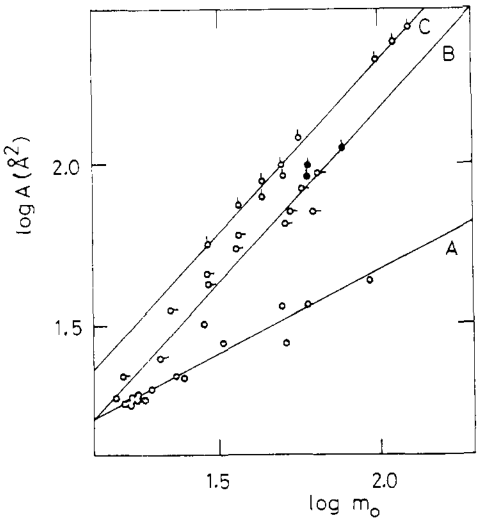

Figure 1. Dependence of the chain cross-sectional area, A, on the mass per main-chain bond, m_0, for EC (open circles), HC$_1$ (pips right), and HC$_2$ (pips up) polymer series.

Finally, subsituting the above expressions for A into eq 1, one gets for the EC, HC$_1$, and HC$_2$ series, respectively

$$v_c/d_0N_A = 4.65m_0^{-0.5} \tag{3a}$$

$$v_c/d_0N_A = 1.41 \tag{3b}$$

$$v_c/d_0N_A = 2.05 \tag{3c}$$

The empirical eq 2 and 3 might serve for a preliminary estimate of chain conformation in the crystalline state for polymers with very bulky side groups, which quite often have very low degrees of crystallinity prohibiting the reliable assessment of X-ray data. To illustrate this thesis, we will choose poly(N-vinylcarbazole), whose X-ray texture diagram does not allow unambiguous determination of the identity period in the chain direction.[14] Now, substituting $m_0 = 96.5$ for this polymer into eq 2a, one finds that the best agreement with the experimental value of interchain distance a = 12 Å[14-16] is obtained from eq 2b for HC$_1$ polymers ($a = (1.41 \times 96.5)^{0.5}$ = 11.6 Å), i.e., for 3/1 or 7/2 helices. Substituting further a typical value d_0 = 1.05 Å for these conformations into eq 3b, one obtains v_c = 0.891 cm^3/g, which should be compared with the experimental figure,[16] v_c = 0.838 cm^3/g. On the other hand, substitution of Crystal's value,[15] d_0 = 7.44/6 = 1.24 Å, into eq 3b yields v_c = 1.053 cm^3/g, which is about 25% high. Thus, empirical equations obtained in this work should prove useful for checking the self-consistency of the experimental X-ray data.[17]

Before concluding, a brief commentary on Boyer et al.'s claim that A is a single parameter controlling the "critical" (entanglement) molecular mass, M_c (or, more precisely, critical number of main-chain bonds, $N_c = M_c/m_0$), for flexible-chain polymers[4,5] is in order. So far, the following empirical equations for N_c were proposed:[18-21]

$$N_c = Xv_a/\langle s^2\rangle_0/M \tag{4a}$$

$$N_c = 3.8V_g^2/m_0 \tag{4b}$$

$$N_c = (0.14/K_0)^2/m_0 \tag{4c}$$

$$N_c = 240(a/\sigma)^{2.5} \tag{4d}$$

In the above equations $X = 400 \times 10^{-17}$ is the "universal" constant introduced by Fox,[18] $\langle s^2\rangle_0$ is the mean-square gyration radius of an unperturbed polymer coil, v_a is the melt specific volume, V_g is defined[19] as the molar volume (in Å^3) of a "chain structural unit about 2.5 Å long", K_0 is the parameter from the Kuhn–Mark intrinsic viscosity equation for perfect solutions,[20] and σ is the stiffness parameter of an isolated macromolecule.[21] Equation 4a can be simplified,[21] writing first $N_c = XV_a/\langle s^2\rangle_0$ (where $V_a = v_aM$ is the melt molar volume) and using the approximation $V_i = na^2\,l$ (where l is the length of a single bond and n is again the number of main-chain bonds in the chain repeating unit) for a van der Waals volume of repeating unit. Writing then $V_aK_a = V_iN_A$ (where K_a = constant is the packing coefficient in the amorphous state[21]) and taking into account that $\langle s^2\rangle_0 = (\text{constant})\langle h^2\rangle_0 = (\text{constant})Nl^2\sigma^2$ (where $\langle h^2\rangle_0$ is the mean square, end-to-end distance of a macromolecule), one obtains from eq 4a approximately $N_c = (\text{constant})(a/\sigma)^2$ which is virtually identical to eq 4d. Moreover, substituting $K_0 = \Phi[\langle h^2\rangle_0/M]^{3/2}$ (where Φ is the Flory parameter) and using the same approximations as before, one gets from eq 4c $N_c = (\text{constant})(m_0/\sigma^3)^2$ which after substitution of eq 2 above yields for EC, HC$_1$, and HC$_2$ the polymer series

$$N_c = (\text{constant})(a^4/\sigma^3)^2 \tag{5a}$$

$$N_c = (\text{constant})(a^2/\sigma^3)^2 \tag{5b}$$

$$N_c = (\text{constant})(a^2/\sigma^3)^2 \tag{5c}$$

On the other hand, assuming[21] $V_g = a^2 \times 2.5$ (Å^3) and again making use of eq 2, one obtains from eq 4b for different series:[22]

$$N_c = \text{constant} \tag{6a}$$

$$N_c = (\text{constant})a^2 \tag{6b}$$

$$N_c = (\text{constant 2})a^2 \tag{6c}$$

It follows from the foregoing analysis that eq 4a, 4c, and 4d, which explicity take into account the conformational characteristics of individual macromolecules, predict the (generally equal to or higher than) second-power dependence of N_c on the ratio of chain thickness and stiffness parameter. One can, of course, make a further simplification, recalling that σ depends on the crystalline volume per main-chain bond, V_c/m_0,[11] and thus obtain a $N_c \sim (a)^m$-like dependence (where m is an empirical parameter) similar to eq 6a–c above or to that proposed by Boyer et al.[4,5] However, in view of a drastic conformation dependence of both a and σ, a universal relation between N_c and a with a unique set of numerical constants seems hardly probable. A similar argument should also apply for a possibility of correlation between a and σ.[5,23]

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(23) Substituting $V_c/m_0 = Ad_0$ into equations[11] $V_c/m_0 = 14\sigma$ and $V_c/m_0 = 4.4\sigma^{3.5}$ for the EC and HC series, respectively, one obtains, log σ = log A − 1.042 and log σ = −0.184 + 0.286 log A, which should be compared to Boyer et al.'s result,[5] log σ = 0.38 + 0.22 log A. It appears, therefore, that the latter expression would apply at best only to HC polymers.

Linear Viscoelasticity in Gaussian Networks

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ABSTRACT: The relaxation spectrum at long times has been calculated for tree-like networks of Gaussian strands in which all strands have the same length and all junctions have the same functionality F. The phantom network approximation has been used, so entanglement effects are not included. As in an earlier analysis of the equilibrium elasticity of networks, the calculations were performed in two steps. The spectrum for an ensemble of arbitrarily large sample networks with peripheral junctions anchored at their most probable distribution of locations was obtained, then the contribution associated with elements far removed from the peripheral junctions was extracted. The resulting spectrum is continuous and becomes narrower with increasing functionality. The maximum relaxation time is $\tau_0/(1 - 2(F - 1)^{1/2}/F)$ in which τ_0 is the primary relaxation time of unattached strands. Thus, even in the most extreme case of trifunctional junctions ($F = 3$), the longest relaxation time is smaller than $20\tau_0$, indicating the need to consider additional structural features, such as dangling strands and entanglements, to account for the much broader relaxation spectra of real networks.

Recently we proposed a model for dealing with equilibrium elasticity in Gaussian networks which uses the properties of small sample networks.[1,2] These micronetworks consist of Gaussian strands which are joined by mobile junctions. They are anchored at the periphery by other junctions which move affinely with macroscopic deformations. The micronetworks have no internal loops, consistent with the locally tree-like connectivity of most real networks. They are free to assume any configuration, regardless of the state of their environment, so effects such as entanglement or association are not included.

The free energy of deformation for an ensemble of micronetworks was found to consist of two terms, one proportional to the number of strands joining two mobile junctions (internal strands), the other proportional to the number of strands joining a mobile junction and a fixed junction (peripheral strands). The free energy of deformation for macroscopic networks, in which all junctions are mobile, was assumed to be associated with the term in the micronetwork expression applying to internal strands, with the following result for volume-preserving deformations.

$$\Delta A = (S - J)kT\left[\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2}\right] \qquad (1)$$

The quantities S and J are the number of elastically active strands and the number of junctions in the network; α_x, α_y, and α_z are the extension ratios along the principal axes of deformation.

In this article we apply the same model to the calculation of linear viscoelastic behavior in networks. The relaxation spectrum $H(\tau)$ is calculated for micronetwork ensembles by the procedure of Zimm[3] for the case of no hydrodynamic interaction ($h = 0$). The spectrum associated with portions of the network which are remote from the fixed points is then extracted and applied to macroscopic networks. The equilibrium and relaxation problems are related since each depends on the eigenvalues of a matrix defined by the structure of the network. However, equilibrium elasticity depends only on the number of eigenvalues, while relaxation behavior also depends on their magnitudes. Thus ΔA depends only on the total number of strands and junctions, while $H(\tau)$ also depends on strand length distribution and the distribution of junction functionalities. Also, the separation of the contribution of fixed junctions to relaxation behavior turns out to be less straightforward than that in equilibrium elasticity because the effects of fixed junctions on $H(\tau)$ extend well into the micronetwork interior.

We consider here only the simplest possible structure with tree-like local connectivity: all strands have the same contour length, and all junctions have the same functionality. Interactions between the network and its surroundings are characterized merely by a frictional coefficient. Attributes of real networks such as dangling structures are not considered. Eventually we hope to extend the calculations to deal with dangling structures which, in combination with entanglement effects, appear to be mainly responsible for the long relaxation times of lightly cross-linked networks.[4,5] Since long time processes are the principal interest we will omit intra-strand relaxations entirely.

Background

Several years ago Chompff and co-workers published a series of papers on relaxation in tetrafunctional net-

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