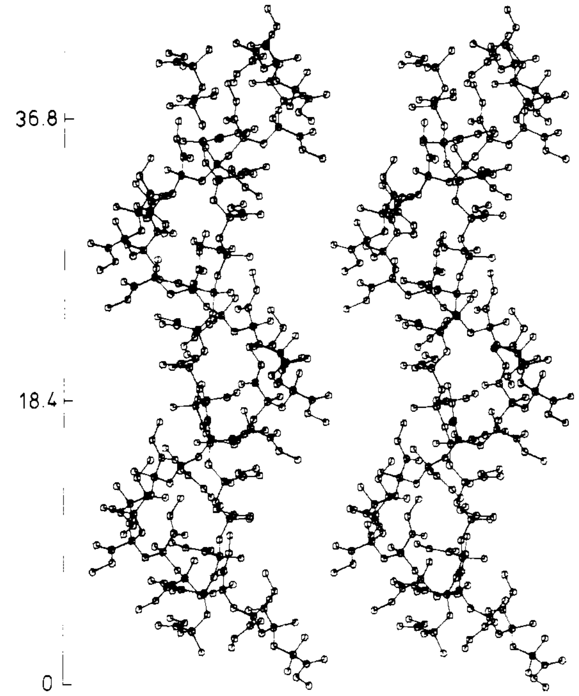

Figure 4. Stereoview of the stereocomplex of it- and st-PMMA (distances are given in Å).

Therefore, the stereocomplex formation can take place with it-PMMA and several syndiotactic methacrylic chains. The packing of different stereocomplex chains in a unit cell must be regarded as a hexagonal packing of rods, comparable with that of it-PMMA. However, the chains are not only shifted but also rotated with respect to each other to obtain a good steric fit. Therefore in the equatorial reflections no systematic extinctions, as in the case of it-PMMA, occur.

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Temperature Coefficients of Unperturbed Chain Dimensions. Helical Wormlike Chains

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In a series of papers on the helical wormlike (HW) chain,[1,2] we have shown that it can mimic the equilibrium conformational behavior of real chains as well as the rotational isomeric state (RIS) model.[3] In the study of chain conformations, the temperature coefficients of unperturbed chain dimensions along with the characteristic ratios provide valuable information, and both are the primary subjects of theoretical evaluation on the basis of the RIS model. In this note, therefore, we make a further test of the validity of the HW model with respect to the temperature coefficient of the mean-square end-to-end distance. Besides this, it is necessary to establish the temperature dependences of the model parameters in order to evaluate, for instance, the activation energies for local chain motions on the basis of the (discrete) HW chain.[4]

We consider the HW chain of contour length L. The basic model parameters are the constant curvature κ_0 and torsion τ_0 of its characteristic helix,[1] the stiffness parameter λ^{-1}, and Poisson's ratio σ of the chain as an elastic wire. λ^{-1} is defined by

$$\lambda^{-1} = 2\alpha/kT \tag{1}$$

where α ($=\pi d^4E/64$) is the bending force constant (with d the diameter of the cylindrical wire and E Young's modulus), k is the Boltzmann constant, and T is the absolute temperature. We assume that $\sigma = 0$, as in most of the cases studied previously and, for convenience, measure L, κ_0^{-1}, and τ_0^{-1} in units of the length λ^{-1}

$$\begin{aligned} L &= \lambda L' \\ \kappa_0 &= \lambda^{-1}\kappa_0' \\ \tau_0 &= \lambda^{-1}\tau_0' \end{aligned} \tag{2}$$

the primed quantities being unreduced. Then the coil limiting value $\langle R^2\rangle_C$ of the (unreduced, unperturbed) mean-square end-to-end distance $\langle R^2\rangle$ is given by[1,2]

$$\begin{aligned} \langle R^2\rangle_C/L &\equiv \lim_{L\to\infty} (\langle R^2\rangle/L) \\ &= (4 + \tau_0^2)/(4 + \kappa_0^2 + \tau_0^2)\lambda^2 \end{aligned} \tag{3}$$

Now, as far as the hypothetical elastic wire model is adopted, the temperature coefficients of L', $\kappa_0'^{-1}$, and $\tau_0'^{-1}$ must be of the same order of magnitude as linear thermal expansion coefficients of ordinary solids (10^{-6}–10^{-5} deg $^{-1}$), so that their temperature dependences may be ignored completely. Then, if we assume that α is also independent of temperature, we have

$$\frac{\mathrm{d}\ln\langle R^2\rangle_C}{\mathrm{d}T} = -\frac{16 - 4\kappa_0^2 + (8 + \kappa_0^2 + \tau_0^2)\tau_0^2}{(4 + \tau_0^2)(4 + \kappa_0^2 + \tau_0^2)}T^{-1} \tag{4}$$

In the sixth column of Table I are given values of the temperature coefficient calculated from eq 4 at given temperatures (in the fifth column) with the values of the model parameters (in the second and third columns) determined previously[1,2,5–7] for polymethylene (PM), poly(dimethylsiloxane) (PDMS), poly(oxymethylene) (POM), isotactic and syndiotactic polypropylene (i- and s-PP), isotactic and syndiotactic polystyrene (i- and s-PS), isotactic, atactic, and syndiotactic poly(methyl methacrylate) (i-, a-, and s-PMMA), and poly(DL-alanine) (PDLA). The observed values[8–11,13–19] are given in the last column, where the values for POM are the RIS ones.[12] The agreement between the calculated and observed values is rather good for some of them, but not always for others. However, the assumption that α is independent of T seems valid as a first approximation for these ordinary flexible polymers. We note that for the Kratky–Porod (KP) wormlike chain,[20] which is a special case of the HW chain with $\kappa_0 = 0$, the

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Table I

Model Parameters and Temperature Coefficients of Unperturbed Chain Dimensions for Various Polymers

polymer	κ_0	$\lvert\tau_0\rvert$	λ^{-1}, Å	T, K	$10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$, deg^{-1} calcd	$10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$, deg^{-1} obsd
PM	0.3[a]	0[a]	14.5[a]	413	−2.3	−1.2 to −1.0 (383–463 K)[f]
PDMS	2.6[b]	0[b]	20.7[b]	298	0.86	0.71–0.78 (313–373 K)[g]
POM	17[a]	25[a]	15.6[a]	303	−3.3	−2.6 to −0.46 (473 K)[h]
i-PP	3.5[c]	4.5[c]	14.2[c]	413	−2.2	−1.5 (~416 K)[i]
s-PP	7.5[c]	30[c]	26.2[c]	413	−2.4	−0.7 (~318 K)[j]
i-PS	11[a]	15[a]	26.4[a]	300	−3.3	
a-PS						−0.1 (293–427 K)[k]
s-PS	0.8[a]	2.3[a]	40.4[a]	300	−3.2	
i-PMMA	1.7[a]	1.4[a]	32.7[a]	300	−1.9	−2.3 (303–425 K)[l]
a-PMMA	2.75[d]	0.6[d]	44.6[d]	300	0.55	~0 (303–343 K)[m]
s-PMMA	4.4[a]	0.8[a]	65.6[a]	300	1.3	1.4 (307–378 K)[l]
PDLA	6.5[e]	0[e]	28.3[e]	300	2.8	

[a] See ref 5. [b] See ref 6. [c] See ref 1. [d] See ref 2. [e] See ref 7. [f] See ref 8–10; see also ref 3, p 45. [g] See ref 11; see also also ref 3, p 46. [h] RIS values; see ref 12. [i] See ref 13. [j] See ref 14. [k] See ref 15. [l] See ref 16 and 17. [m] See ref 17–19.

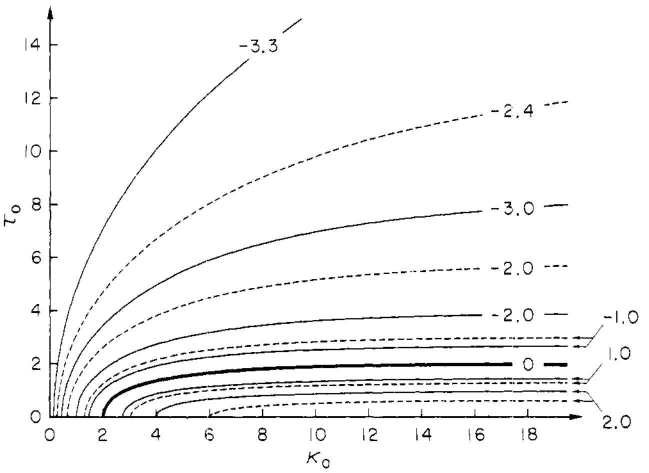

Figure 1. Contour map of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$ in a (κ_0, τ_0) plane. The full and broken curves are the contour lines at $T = 300$ and $T = 400$ K, respectively.

temperature coefficient is always equal to $-T^{-1}$ on the present assumption, as seen from eq 4.

It is interesting to see that the temperature coefficient is positive for PDMS, s-PMMA, and PDLA. In this connection, a contour map of the temperature coefficient in a (κ_0, τ_0) plane calculated from eq 4 is shown in Figure 1, where the full and broken curves are the contour lines at $T = 300$ and 400 K, respectively, the attached numbers indicating the values of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$. Along the heavy full curve 0, it vanishes at all temperatures. Comparing Figure 1 with Figure 3 of ref 21 or Figure 2 of ref 22, we see that the temperature coefficient becomes positive for typical HW chains. This is not difficult to understand, considering the fact that typical HW chains have locally *bent* backbones, which are straightened as the temperature is increased.

Our final remark is concerned with cellulose derivatives, for which observed values of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$ are −7 to −3 deg^{-1}.[23] These large negative coefficients cannot be explained by means of eq 4 even if we assume the KP chain ($\kappa_0 = 0$), for which the negative temperature coefficient becomes a maximum in magnitude. This difficulty may be removed by taking into account the dependence of the force constant α on temperature. Then the factor T^{-1} on the right-hand side of eq 4 is replaced by $T^{-1} - \mathrm{d}\ln\alpha/\mathrm{d}T$. Thus we find that $10^3(\mathrm{d}\ln\alpha/\mathrm{d}T) \simeq -4$ to 0 deg^{-1} for cellulose derivatives (at $T \simeq 300$ K) if the KP chain is assumed. This result seems reasonable since it means that the temperature coefficient of Young's modulus is negative. However, it is difficult and also meaningless to give any more physical interpretation to such temperature coefficients of α.

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Kinetics of Polymer Complex Interchange in Poly(acrylic acid)–Poly(oxyethylene) Solutions

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Received June 8, 1982

Poly(acrylic acid) (PAA) and poly(oxyethylene) (POE) have long been known to form complexes in water solution.[1] Osada has studied the equilibrium of this process by using the pH shift accompanying complex formation.[1b] He has demonstrated the cooperativity of the association by the steep dependence of the complex stability on the chain length of the interacting polymers.

We have initiated a study of this complex by taking advantage of the emission characteristics of the dansyl moiety, which fluoresces much more intensely in organic media than in water.[2] We have found that aqueous solutions of dansyl-labeled PAA exhibit a large increase of fluorescence on complexation with POE, reflecting the