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(9) We have taken the ^{13}C spectra of poly(γ-hydroxy-L-proline) in 4 and 6 M $CaCl_2$ and in 6 and 8 M LiBr. These spectra will be reported at a later date. In each of the four spectra a major and a minor resonance for each of the C^{γ} and C^{β} atoms are clearly visible. The minor resonance for the C^{γ} atom in both of the aqueous salt solutions is 2.2 ppm upfield from the major C^{γ} trans resonance. The minor resonance for the C^{β} atom is between 2.1 and 2.3 ppm downfield from the major C^{β} trans resonance.

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(19) It has been previously reported that the ^{13}C spectrum of poly(γ-hydroxy-L-proline) in 6 M LiBr solution only shows the presence of the trans isomer.[10] However, the signal-to-noise ratio in this earlier work[10] is sufficiently low so that the cis resonance would be easily obscured. The implication that no isomerization occurs is thus not correct.

Semiempirical Distribution Functions for Linear and Circular Gaussian Chains

C. D. HOWELL and B. E. EICHINGER*

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195.

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The known exact distribution functions of the three-dimensional radius of gyration for large linear chains[1-3] and for circular chains of any length[4] are complicated functions. In the first case, the distribution function $P(s)\,ds$ is given as an infinite sum of modified Bessel functions, and for the second case $P(s)\,ds$ for large chains is given by an infinite sum of polynomial and exponential functions of s^2. These functions are difficult to manage, since virtually all manipulations with them must be done numerically. Since distribution functions are applied to various problems,[5,6] it is expedient to find simple approximations to the exact functions which can be (i) easily manipulated and are (ii) reasonably accurate.

Table I

Chain	Constant	a	β
Circular	405.9	0.74	5/4
Linear	11.68	0.23	17/10

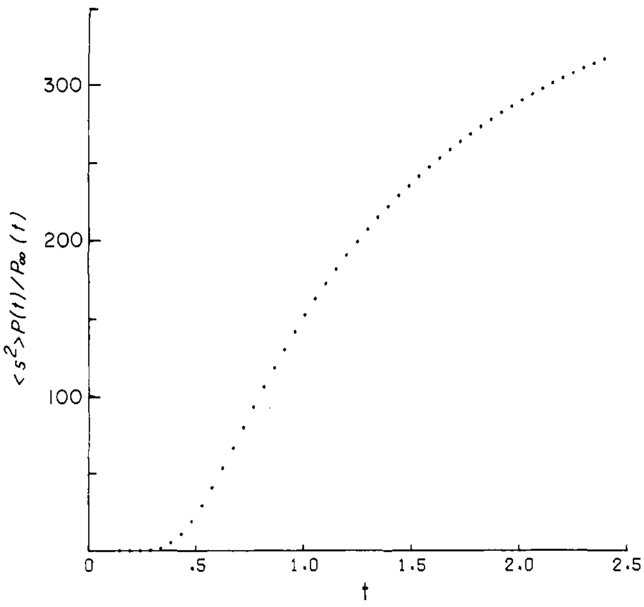

Figure 1. The unnormalized ratio $\langle s^2\rangle P(t)/P_\infty(t)$ for the circular chain.

The general features of distribution functions which have emerged recently[7] suggest that their binodal character is controlled by the asymptotic part of $P(s)$, here called $P_\infty(s)$. To test this conjecture, we have computed the exact distribution functions $\langle s^2\rangle P(t)\,dt$, where $t = s^2/\langle s^2\rangle$ and $\langle s^2\rangle$ is the mean square (unperturbed) value of s, for both circular[3] and linear chains,[4] and have formed the ratio $P(t)/P_\infty(t)$. For the circular chain[4,7] the unnormalized

$$P_\infty(t) = t^2 \exp(-\pi^2 t/2) \qquad (1)$$

and for the linear chain[1,7] the corresponding function is

$$P_\infty(t) = t^{1/2} \exp(-\pi^2 t/4) \qquad (2)$$

The unnormalized ratio $P(t)/P_\infty(t)$ for the circular chain is shown in Figure 1. The corresponding function for the linear chain has similar behavior but is not shown. These functions bear strong resemblance to tanh $(1/t)$ as encountered in the Ising problem.[8] Thus, we were led to attempt to fit $P(t)$ by

$$\langle s^2\rangle P(t) = \text{const}[1 - \tanh\,(a/t^{\beta})]P_\infty(t) \qquad (3)$$

where a and β are adjustable and $P_\infty(t)$ is given by eq 1 or eq 2 as appropriate. Values for the normalization constant, a, and β for both linear and circular chains selected to give the best fit near the maxima are given in Table I. Figures 2 and 3 graphically display the quality of the fit of the approximate functions to be exact. In Table II, the first few moments of t calculated from eq 3 are compared with exact values. The moments are generally accurate to within a few tenths of a percent. (The agreement between the approximate and exact moments could be made better by slight changes in a and β. However, specification of these parameters with an accuracy

Table II

Chain	Moment	Exact[a]	Approx	% dif
Circular	$\langle t\rangle = \langle s^2\rangle/\langle s^2\rangle$	1.0000	0.9982	0.2
	$\langle t^2\rangle = \langle s^4\rangle/\langle s^2\rangle^2$	1.1333 = 17/15	1.1296	0.3
	$\langle t^3\rangle = \langle s^6\rangle/\langle s^2\rangle^3$	1.4508 = 457/315	1.4430	0.5
Linear	$\langle t\rangle$	1.0000	1.0048	0.5
	$\langle t^2\rangle$	1.2667 = 19/15	1.2718	0.4
	$\langle t^3\rangle$	2.0032 = 631/315	2.0055	0.1
	$\langle t^4\rangle$	3.8698 = 1219/315	3.8603	0.3

[a] Exact moments for the circular chain were calculated from sums given by Šolc, ref 4, with expressions for cumulants given in ref 9. Values for the linear chain were taken from ref 5.

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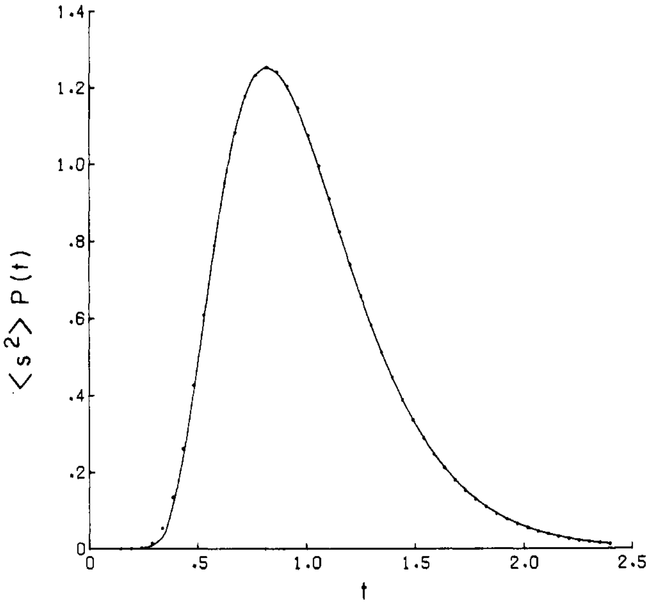

Figure 2. Distribution function of the reduced squared radius of gyration $t = s^2/\langle s^2\rangle$ for the circular chain as a function of t for large n. The solid curve is calculated from the exact distribution function given in ref 4. The points are values given by the empirical eq 3, with parameters listed in Table I.

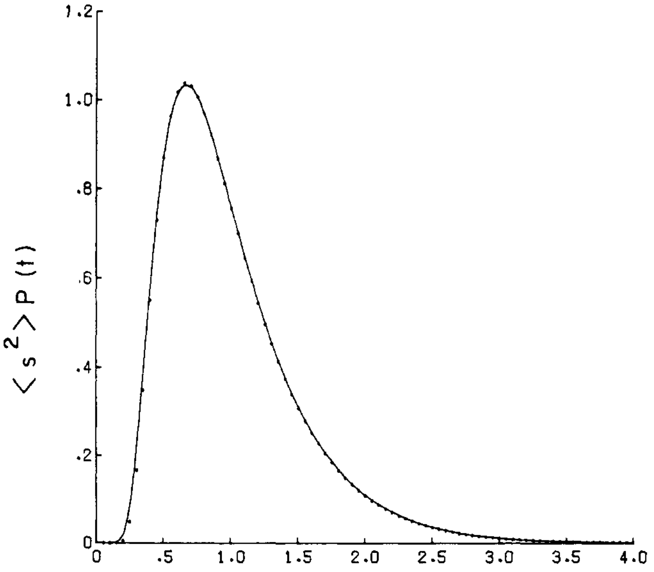

Figure 3. Distribution function for the linear chain. Exact curve calculated from ref 2. Otherwise the same as Figure 2.

greater than 1% is unwarranted in the spirit of approximation or in view of conceivable applications.)

The approximate function given by eq 3 suffers in that it can only be integrated numerically. However, a simple one-line FORTRAN statement suffices to evaluate the function. The numerical integrations required to construct Table II were accomplished with the International Mathematical and Statistical Libraries, Inc. (IMSL) program DCADRE, which uses cautious Romberg extrapolation.[10] Calculations were performed on the University of Washington CDC 6400 computer.

Although the approximate function is not easily integrable, it is readily differentiated. It is expected that functions of this class will find application to rubber elasticity,[6] should they be useful descriptions of the distribution functions of more complicated molecules.

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Bimodal Closed Cloud Point Curves of Ternary Systems

SHAUL M. AHARONI

Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960. *Received August 22, 1977*

There are several recent literature reports indicating bimodal cloud point curves (CPC) for polymer–polymer systems[1,2] and for ternary polymer–polymer–solvent (components 2, 3, and 1, respectively) systems.[1,3–6] Koningsveld et al.[1] explain the bimodal shape of the CPC as caused by a particular concentration dependence of the free enthalpy parameter, g. Welygan and Burns[4] present an explanation for the bimodal shape of the CPC in a ternary system, but the scarcity of data points and their scatter preclude a verification of the validity of the model. In this note we wish to report another ternary system that shows a bimodal shape of the CPC. This system is comprised of two compatible polymers and a solvent. The results obtained by changing solvents, and from the use of a mixed solvent, may aid in a better understanding of bimodal cloud point curves.

The two polymeric components in our study are a copolyester and an epoxy system with a very broad molecular weight (M) distribution. The copolyester was prepared by melt polymerization to have the molar composition of 65:30:5 terephthalate/isophthalate/sebacate with 70:20:10 ethylene glycol/resorcinol di(β-hydroxyethyl) ether/poly(tetramethylene ether) glycol with M_n of 1000. The resultant copolyester had a glass transition temperature, T_g, of −3 °C, was found by x-ray techniques to be amorphous, and had an intrinsic viscosity in 60:40 tetrachloroethane/phenol in the order of 1.1–1.3 (depending on the batch). This polymer was found to be compatible with an epoxy system composed of 50 wt % 1:1 copolymer of bisphenol A and epichlorohydrin (Union Carbide's Phenoxy PKHH grade, $M_w \sim 80\,000$, $M_n = 23\,000$), 40% intermediate M epoxy (diglycidyl ether of bisphenol A, Ciba-Geigy Araldite 6099 grade with $M_w \sim 5000$–8000), and 10% low M epoxy (diglycidyl ether of bisphenol A, Ciba-Geigy Araldite 6010 grade, $M_w = 370$–390). This epoxy system is a transparent solid whose T_g is 85 °C and which is completely amorphous.

Intimate mixtures of the two components covering the range of 1:3 to 3:1 ratios were prepared by several means, as described by Aharoni and Prevorsek.[7] When a small amount of solvent (in the order of 5%) remained trapped in the solid mixture, dense polyester particles of ~5000 Å in diameter were

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