Random-Coil Dimensions of Poly(trimethylene oxide), an Unusually Compact Chain Molecule

Y. Takahashi and J. E. Mark*[1]

Contribution from the Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48104. *Received November 18, 1975*

Abstract: Poly(trimethylene oxide) $[CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_x$, prepared by the ring-opening polymerization of oxacyclobutane, was studied with regard to its characteristic ratio $\langle r^2\rangle_0/nl^2$, where $\langle r^2\rangle_0$ is the unperturbed dimension of the chain in the random-coil state, n is the number of its skeletal bonds, and l^2 is the average square of their length. Viscometric and osmometric results obtained on fractions of the polymer in benzene at 30 °C indicate that this chain molecule has the smallest value of $\langle r^2\rangle_0/nl^2$ of any polymer thus characterized to date. This unusual compactness can be attributed to a high degree of conformational randomness in the chain, in that the two C–C skeletal bonds in the repeat unit are preferentially in gauche rotational states whereas the two C–O bonds are preferentially in trans states. This explanation in terms of randomness of conformations is supported by the fact that, according to force–temperature measurements on networks of poly(trimethylene oxide) in the amorphous state, the unperturbed dimensions of this chain molecule are very nearly independent of temperature. It is also supported by the fact that poly(trimethylene oxide) has the lowest melting point of any member of the polyoxyalkane series $[(CH_2)_y\text{-}O\text{-}]_x$.

Since many of the unique properties of polymeric materials are a direct result of the multitude of configurations or spatial arrangements a long chain molecule can assume, the interpretation and detailed understanding of chain configurations has become a problem of great interest in polymer science.[2-5] The statistical property presently used most extensively in such studies of spatial configurations is the end-to-end dimension $\langle r^2\rangle_0$ of the chain as unperturbed by excluded volume effects.[2,6] This unperturbed dimension, a measure of the effective size of the molecule in the random-coil state, is usually expressed relative to nl^2, where n is the number of skeletal bonds and l^2 is the average square of their length. The *characteristic ratio* $\langle r^2\rangle_0/nl^2$ thus defined represents the factor by which the actual unperturbed dimensions of the chain differ from those it would have if it were freely jointed. Values of this important ratio have been extensively tabulated for a great variety of chain molecules, with most polymers studied to date yielding values in the range 6–10.[2]

One important general question in this area concerns the factors which can cause a chain molecule to be either highly extended or unusually compact. The factors conducive to high spatial extension have been explored rather thoroughly.[2-5] Chain molecules tend to have highly extended configurations when structural features restrict the chain backbone to one conformation, or a small number of conformations, generally helical and of high spatial extension. Such restriction can occur because of (i) steric interferences between relatively bulky groups, as is for example the case in isotactic polystyrene[5,7,8] and isotactic poly(*tert*-butylethylene oxide),[9] (ii) strong attractive forces, such as the coulombic and London dispersion forces occurring in polyoxymethylene,[2] and (iii) actual chemical bonding resulting in the formation of ring structures about the chain backbone, as is the case in poly-L-proline[2] and various cellulose derivatives.[3,10]

Although the conformational factors conducive to compactness in chain molecules have not been discussed as explicitly, some generalizations can be drawn from the experimental and theoretical information presently at hand. In some cases, the conformational regularity obtained by partially restricting a chain molecule to a small number of conformational states can result in unusually small chain dimensions. One notable example would be poly(diphenylsiloxane) $[Si(C_6H_5)_2\text{-}O\text{-}]_x$ and isotactic poly(methylphenylsiloxane) $[Si(CH_3)(C_6H_5)\text{-}O\text{-}]_x$,[11] where x is the degree of polymerization. In these molecules, the very favorable phenyl–phenyl interactions would stabilize trans conformations which, because of the inequality of bond angles about the Si and O atoms, would correspond to very small end-to-end dimensions. Another example would be the totally unencumbered chains of sulfur $[S\text{-}]_x$ and selenium $[Se\text{-}]_x$. Here the relatively long S–S and Se–Se bonds, the complete absence of pendant groups, and the strong London dispersion forces all contribute to the stabilization of regular conformations of very small spatial extension.[2] Unfortunately, relatively few experimental results are presently available for molecules of this type.

A statistically more interesting type of compact chain molecule is one in which there is a very high degree of conformational *irregularity* or randomness, as exemplified by the idealized freely rotating chain.[2,6] A less hypothetical example of this type of molecule is poly(dimethylsilmethylene) $[Si(CH_3)_2\text{-}CH_2\text{-}]_x$;[12,13] since methyl groups and methylene groups are very nearly identical in their intramolecular interactions,[2,14] trans and gauche rotational states about the skeletal bonds in this molecule have very nearly the same probability of occurrence.[13] As a consequence, the characteristic ratio of this molecule has the rather small value, 5.32 ± 0.01.[12] A different type of conformational randomness would be expected to occur in the poly(trimethylene oxide) chain $[CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_x$, a portion of which is shown in Figure 1. The two C–C skeletal bonds in the repeat unit of this molecule exhibit a preference for gauche states, while the remaining two C–O bonds have a preference for trans states.[2,15,16] There is thus a high degree of conformational randomness upon averaging over the entire repeat unit. In this sense, poly(trimethylene oxide) is unique in the polyoxyalkane series $[(CH_2)_y\text{-}O\text{-}]_x$, the first member of which is polyoxymethylene $[CH_2\text{-}O\text{-}]_x$ ($y = 1$), in which the skeletal bonds all have a preference for gauche states, thus giving rise to spatially extended helical sequences,[2] and the last of which is polyethylene $[CH_2\text{-}CH_2\text{-}]_x$ ($y = \infty$), in which all skeletal bonds have a preference for trans states, giving planar zig-zag conformations, also of very high spatial extension.[2]

Because of this unusual feature of the poly(trimethylene oxide) chain, the present study was undertaken to obtain values of its unperturbed dimensions by means of viscometric and osmometric measurements on the polymer in dilute solution. The temperature dependence of these dimensions will also be obtained by stress–temperature measurements on networks of the polymer in the amorphous state. The latter quantity is of interest since the effect of temperature on the distribution of conformations about the pair of C–C skeletal bonds in poly(trimethylene oxide) should be largely offset by its opposite

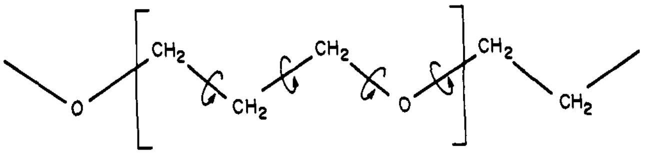
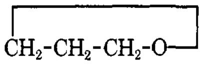


Figure 1. A segment of the poly(trimethylene oxide) chain shown in the planar, all-trans conformation. The brackets enclose the four-bond repeat unit of the chain.

effect on the pair of C-O bonds, and thus the unperturbed dimensions of this molecule would be expected to be relatively insensitive to temperature.

Experimental Section

Polymer Synthesis and Fractionation. The monomer oxacyclobutane



obtained from the Aldrich Chemical Co., was purified by refluxing over KOH and then CaH_2, under an inert atmosphere of N_2, followed by vacuum distillation. It was polymerized at −78 °C, both in the undiluted state and in CH_3Cl solution, using BF_3 as catalyst.[17,18] The concentrations of monomer, solvent, and catalyst and the reaction times were varied so as to give as wide a range of molecular weights as possible. A total of 13 polymerizations carried out in this manner had values of the percent conversion ranging from 12 to 93%, and gave samples of poly(trimethylene oxide) having values of the intrinsic viscosity[6] $[\eta]$ ranging from 0.5 to 3.3 dl g^{-1}. Each sample of polymer thus prepared was purified by addition of a CH_3OH-NH_4OH solution, precipitation into water, and two reprecipitations of an acetone solution of the polymer, also into water. Finally, each sample was dissolved in benzene, filtered, and freeze-dried. Several of these samples were then combined to give three composite samples sufficiently large to separate into fractions.

Three fractionations and one sub-fractionation were carried out on these composite samples, using standard methods of fractional precipitation.[6] A rather low temperature of either 30 or 35 °C was employed, in view of the relatively low melting point, 35 °C,[17] of poly(trimethylene oxide). Acetone and distilled water were used as solvent and nonsolvent, respectively, and N_2 was used to provide an inert atmosphere. The separations were observed to involve two liquid phases, as is required to obtain fractionation on the basis of molecular weight.[6] Of a total of 26 fractions thus obtained, ten were chosen for characterization in the present study. They varied in size from 0.4 to 17% of the total polymer charge from which each was obtained, and thus may be assumed to have relatively narrow molecular weight distributions.

Viscometry and Osmometry. Reagent grade benzene, which had been further purified by refluxing and distillation over sodium, was used for both the viscosity and osmotic pressure determinations. All measurements were carried out at a temperature of 30 °C, at which benzene has a density of 0.8684 g cm^{-3}.[19] Viscosities were measured in a Cannon-Ubbelohde viscometer of sufficiently small capillary to make kinetic energy corrections negligible. Osmotic pressures were measured in a high speed osmometer (Melabs CSM-2) containing a gel cellophane membrane (Arro Laboratories type 600W) conditioned for use in benzene.

Network Elasticity. Two small sheets of poly(trimethylene oxide), pressed from one of the unfractionated samples, were cross-linked, under vacuum and at room temperature, using 13.6 Mrads of γ radiation from a ^{60}Co source. The two networks thus prepared were labeled N1 and N2; they were found to contain 11 and 5% soluble material, respectively, upon extraction with benzene. Reswelling in a benzene solution of *N*-phenyl-2-naphthylamine was used to incorporate approximately 2% of this antioxidant into each network. Cross-sectional areas A^* of two test strips cut from N1 and N2 were found to be 0.0300 and 0.0426 cm^2, respectively, in the unswollen unstretched state in the vicinity of 40 °C.

Table I. Viscometric and Osmometric Results[a]

Fraction	$[\eta]$, dl g^{-1}	$10^{-5}M_n$, g mol^{-1}	$10^3 A_2$, cm^3 mol g^{-1}	α^b	$\langle r^2\rangle_0/nl^2$
F1	0.849	0.535	2.883	1.681	3.40
2	1.011	0.651	2.548	1.601	3.94
3	1.248	0.875	2.417	1.625	3.99
4	1.472	1.091	2.388	1.659	3.97
5	1.659	1.282	2.498	1.735	3.73
6	1.711	1.318	2.440	1.711	3.88
7	2.027	1.530	2.436	1.691	4.23
8	2.090	1.611	2.457	1.717	4.11
9	2.584	2.269	2.336	1.794	3.87
10	3.309	2.925	2.305	1.787	4.23
				Av	3.94 ± 0.17

[a] In benzene at 30 °C. [b] Chain expansion factor.

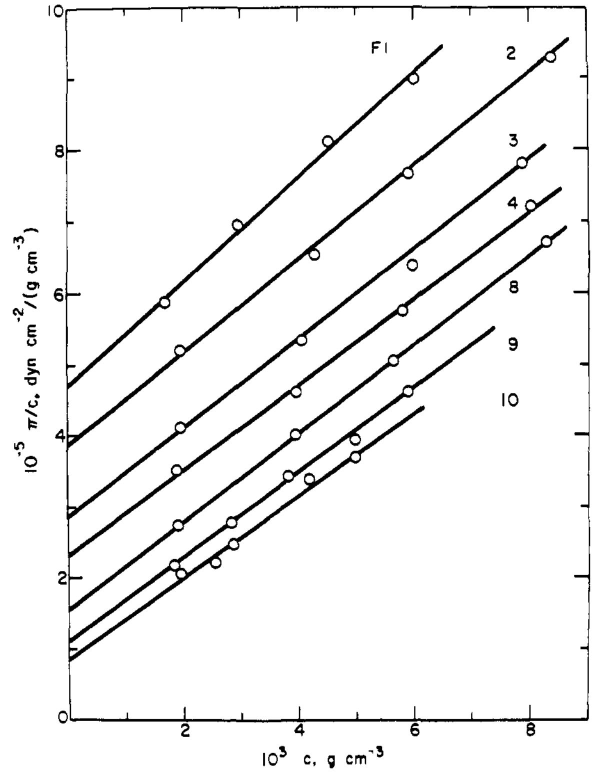


Figure 2. Typical osmotic pressure data obtained on the poly(trimethylene oxide) fractions in benzene at 30 °C.

Stress-temperature measurements were carried out on these test samples in the amorphous, unswollen state, in the usual manner.[20-22] Temperatures were in the range 35-80 °C, and values of the elongation $\alpha = L/L_i$, where L and L_i are the deformed and undeformed lengths of the sample respectively, ranged from 1.22 to 1.96. Values of the stress $f^* = f/A^*$, where f is the elastic force, were first obtained at a series of decreasing temperatures. They were found to be satisfactorily reproduced upon subsequent increase in temperature.

Dilatometric measurements on a sample of amorphous poly(trimethylene oxide) over the range 40-80 °C gave the value 0.73 × 10^{-3} K^{-1} for the thermal expansion coefficient $\beta = (\partial \ln V/\partial T)_p$ in the vicinity of 60 °C.

Results

The Characteristic Ratio $\langle r^2\rangle_0/nl^2$. Values of the intrinsic viscosity $[\eta]$, obtained from the viscosities of the benzene solutions of the polymer at 30 °C in the usual manner,[6] are presented for the ten poly(trimethylene oxide) fractions in the second column of Table I. In the analysis of the osmotic pressures π in benzene at 30 °C, the ratio π/c was observed to vary linearly with the concentration c, as shown by the typical data presented in Figure 2. These data were therefore analyzed by the linear relationship

$$\pi/c = RT(M_n^{-1} + A_2 c) \quad (1)$$

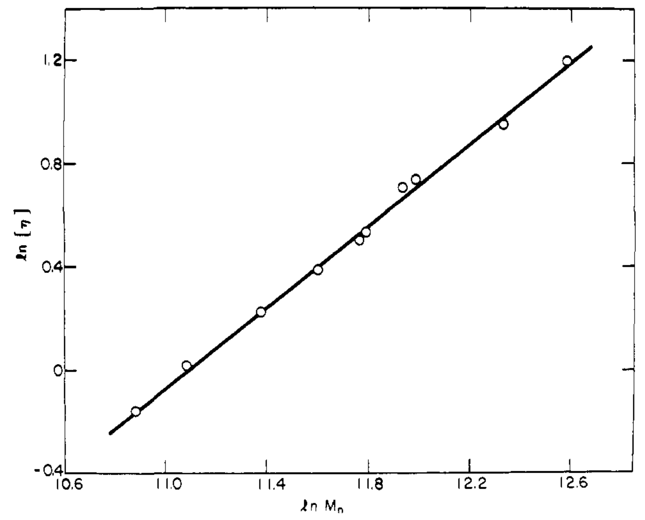


Figure 3. The intrinsic viscosity-molecular weight relationship for poly(trimethylene oxide) in benzene at 30 °C.

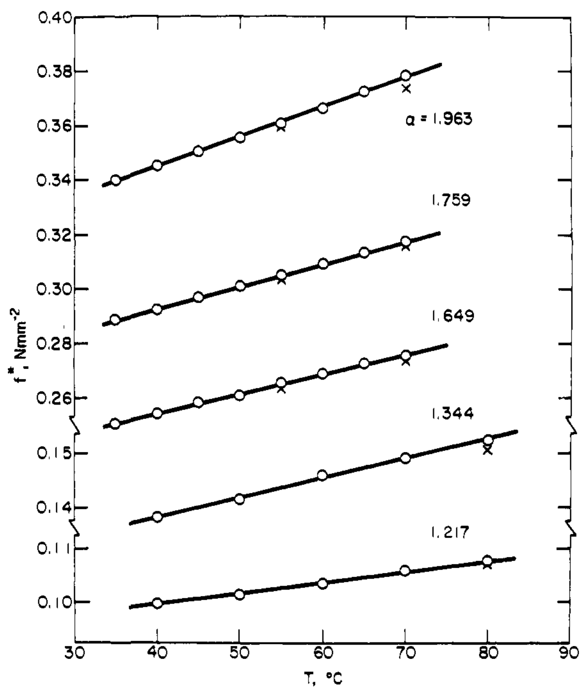


Figure 4. Stress-temperature data obtained on two networks of poly(trimethylene oxide) in the amorphous state. The circles pertain to data obtained upon decrease in temperature, and the X's to data obtained upon subsequent increase in temperature. Each curve is labeled with the appropriate value of the elongation of the network.

where R is the gas constant. Values of the number average molecular weight M_n and second virial coefficient A_2 obtained from the intercepts and slopes, respectively, of these curves are given in columns three and four of the table. The values of A_2 are rather large, and generally decrease with increasing M_n, as expected.[6]

The relationship between $[\eta]$ and M_n is shown logarithmically in Figure 3. The curve shown through the experimental points was located by least-squares analysis, and corresponds to the equation

$$[\eta] = 1.54 \times 10^{-4} M_n^{0.79} \quad (2)$$

for the intrinsic viscosity in dl g^{-1}. This relationship is offered here as an extension or replacement for the approximate relationship[18] $[\eta] = 2.19 \times 10^{-4} M_w^{0.78}$, which also pertains to benzene at 30 °C, but was obtained on unfractionated poly(trimethylene oxide) samples having weight average molecular weights M_w in the relatively narrow range 3 000–28 000.

Table II. Thermoelastic Results[a]

Network	α[b]	$-10^3 [\partial \ln (f^*/T)/\partial T]_{p,L}$	$10^3 \beta/(\alpha^3 - 1)$	$10^3\, \mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T$
N1	1.217	1.05	0.91	0.14
	1.344	0.56	0.51	0.05
N2	1.649	0.38	0.21	0.17
	1.759	0.30	0.16	0.14
	1.963	0.03	0.11	−0.08
				Av 0.08 ± 0.08

[a] On networks in the amorphous state, 35–80 °C. [b] Elongation, or relative length, of the network.

The values of $[\eta]$, M_n, and A_2 reported above were used to calculate values of the chain expansion factor $\alpha = [\langle r^2 \rangle / \langle r^2 \rangle_0]^{1/2}$ which characterizes perturbations due to excluded volume effects.[6] The relationship employed for this purpose was the equation of Orofino and Flory[23]

$$\ln [1 + (\pi^{1/2}/2)(\alpha^2 - 1)] = (27\Phi/2^{5/2}\pi N_{\mathrm{avo}})(A_2 M_n/[\eta]) \quad (3)$$

where Φ is a hydrodynamic constant equal to 2.1×10^{21} dl cm^{-3} mol^{-1} in thermodynamically good solvents,[6,24] N_{avo} is Avogadro's number, and π here is the numerical constant 3.1416. These results are listed in column five of the table. Values of $\langle r^2 \rangle_0$ were then calculated from[6]

$$[\eta] = \Phi[\langle r^2 \rangle_0/M_n]^{3/2} M_n^{1/2} \alpha^3 \quad (4)$$

The average square of the skeletal bond lengths, $l^2 = 2.19$ Å^2, was obtained from l(C–C) = 1.53 Å and l(C–O) = 1.43 Å,[25] and the number of skeletal bonds was calculated from $n = 4(M_n/M_0)$, where $M_0 = 58.08$ is the molecular weight of the repeat unit. Values of $\langle r^2 \rangle_0/nl^2$ thus obtained are presented in the last column of Table I. They are seen to be independent of molecular weight, as expected,[2,6] and give the average value 3.94 ± 0.17 for the characteristic ratio of poly(trimethylene oxide).[26-28]

The Temperature Dependence of $\langle r^2 \rangle_0$. The stress-temperature data obtained on the two poly(trimethylene oxide) networks in the amorphous state are shown in Figure 4. The curves shown were located by least-squares analysis of the data taken in the order of decreasing temperature. Their slopes were used to calculate the values of the coefficient $[\partial \ln (f^*/T)/\partial T]_{p,L}$ listed in the third column of Table II. The following column gives values of the term[20,29] $\beta/(\alpha^3 - 1)$ which takes into account the thermal expansion of the network. Finally, the temperature coefficient of $\langle r^2 \rangle_0$ was calculated from[20,29]

$$\mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T = -[\partial \ln (f^*/T)/\partial T]_{p,L} - \beta/(\alpha^3 - 1) \quad (5)$$

and these results are presented in the last column of the table. The complete set of results indicate that d ln $\langle r^2 \rangle_0$/dT for the poly(trimethylene oxide) chain in the vicinity of 60 °C is $0.08 \pm 0.08 \times 10^{-3}$ K^{-1}.

Discussion

The value of the characteristic ratio found for poly(trimethylene oxide) is compared with the values reported for other $[(\mathrm{CH_2})_y\text{-O-}]_x$ polymers in Figure 5. All results pertain to temperatures in the vicinity of 30 °C. The most reliable of these experimental results are presumably those for polyoxyethylene ($y = 2$),[30] poly(tetramethylene oxide) ($y = 4$),[31] and polyethylene ($y = \infty$),[2,32] since they were obtained in theta solvents, in which excluded volume effects are known to be nullified.[2,6] The points representing these results in the figure

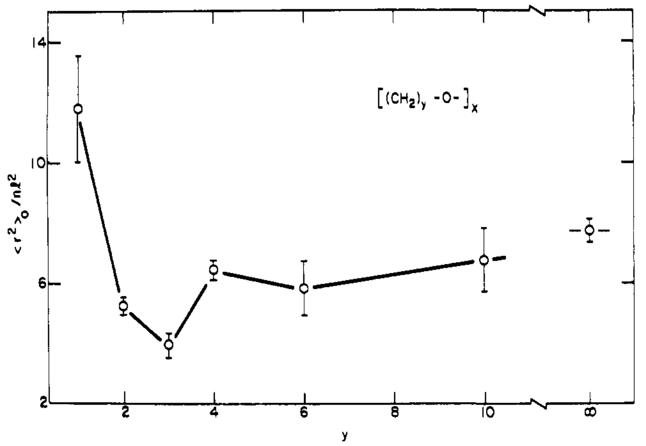


Figure 5. Experimental values of the characteristic ratio for members of the polyoxyalkane series $[(CH_2)_y\text{-O-}]_x$, shown as a function of the number of methylene groups in the repeat unit of the chain. The series begins with polyoxymethylene ($y = 1$) and ends with polyethylene ($y = \infty$).

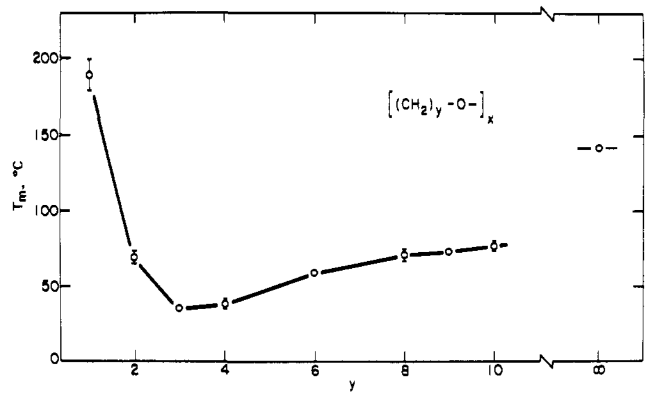


Figure 6. Experimental values of the melting point for members of the polyoxyalkane series;[38] see legend to preceding figure. Each error bar shown specifies the average deviation from the mean value of the melting point, as obtained from a number of studies of the same polymer.

were therefore assigned relatively small error bars, corresponding to an arbitrarily chosen uncertainty of ±5%. In the present study of poly(trimethylene oxide) ($y = 3$), excluded volume effects were not absent and had to be corrected for through knowledge of the second virial coefficient;[23] the resulting value of the characteristic ratio was therefore assigned a larger uncertainty, of ±10%. In the remaining cases, polyoxymethylene ($y = 1$),[33] poly(hexamethylene oxide) ($y = 6$),[34] and poly(decamethylene oxide) ($y = 10$),[35] values of the characteristic ratio were obtained using extrapolation methods[27] of questionable validity,[28] and are uncertain to at least the extent, ±15%, specified for these three points in the figure. The hydrodynamic constant Φ was assigned the value 2.5×10^{21} in the interpretation of the measurements carried out in the theta solvents, and 2.1×10^{21} for the others, carried out in thermodynamically good solvents.[6,24] The entire set of results shows that poly(trimethylene oxide) has the smallest value of $\langle r^2\rangle_0/nl^2$ of any member of the polyoxyalkane series; its characteristic ratio is in fact the smallest observed to date.[2] This compactness is consistent with a high degree of conformational randomness, as anticipated above and now discussed in greater detail.

We consider first those intramolecular interactions occurring between groups separated by three bonds. In polyoxymethylene, these "three-bond" interactions all involve CH_2 groups and O atoms; they are strongly favorable[2,15,16] and give rise to a preference for gauche states, in which the distance of separation of these interacting species is smaller than in the alternative trans state. The two C-O bonds in the polyoxyethylene repeat unit both have a preference for the trans state because of severe $CH_2 \cdots CH_2$ repulsions in the gauche alternatives.[2] The reverse is true for the C-C bond, apparently because of favorable interactions between the relatively small O atoms in the gauche conformation. In poly(trimethylene oxide), states about the two C-C bonds involve $CH_2 \cdots O$ interactions while those about the two C-O bonds involve $CH_2 \cdots CH_2$ interactions.[2,15,16] As a consequence, gauche states are preferred for the first two skeletal bonds in the poly(trimethylene oxide) repeat unit, and trans states for the two others. For $y > 3$, an increasingly large fraction of the skeletal bonds show a preference for trans states. This fraction, which is ⅗ for example in the case of poly(tetramethylene oxide), is given in general by $(y - 1)/(y + 1)$, except for the case of polyoxyethylene, which is the only member of the polyoxyalkane series having a three-bond interaction involving O atoms.[2] Poly(trimethylene oxide) is thus the unique member of the $[(CH_2)_y\text{-O-}]_x$ series in that the number of its skeletal bonds preferring gauche states is the same as that preferring trans. In this sense it is the most conformationally random polyoxyalkane, a characteristic consistent with the unusually low value of its characteristic ratio.

The above arguments are qualitative. A quantitative interpretation of the characteristic ratio of poly(trimethylene oxide) would of course have to take into account the fact that the preference for gauche states about C-C bonds is not nearly as strong as the preference for trans states about C-O bonds.[2,15,16] Also of importance would be "pentane-type" conformations[2] involving $CH_2 \cdots CH_2$ and $O \cdots O$ interactions between groups separated by four bonds. Some preliminary calculations[15] taking quantitative account of both the three-bond and four-bond interactions have been carried out for poly(trimethylene oxide). The range 3.4–4.3 predicted for the characteristic ratio in these calculations is in good agreement with the experimental value 3.9 reported in the present study. More thorough calculations on a number of polyoxyalkanes, including poly(trimethylene oxide), are reported elsewhere.[16]

The fact that the unperturbed dimensions of poly(trimethylene oxide) were found to be essentially independent of temperature is also consistent with the proposed high degree of conformational randomness. An increase in temperature would increase the number of spatially extended trans states in the case of the two C-C bonds in the repeat unit, but would decrease the number of such trans states about the two C-O bonds. The two types of transitions would be partially offsetting, thus making the net effect of temperature on $\langle r^2\rangle_0$ relatively small. More quantitatively, it may be noted that the experimental result $10^3\, d \ln \langle r^2\rangle_0/dT = 0.08 \pm 0.08\ K^{-1}$ is near the lower end of the range 0.9–0.1 K^{-1} predicted for this quantity in the preliminary calculations[15] cited above.

It is also important to mention that poly(trimethylene oxide) has the lowest melting point, $T_m = 35$ °C,[17] of any polymer in the $[(CH_2)_y\text{-O-}]_x$ series.[36-38] Since $T_m = \Delta H_m/\Delta S_m$, the melting point of a substance depends on both the enthalpy of fusion ΔH_m and the entropy of fusion ΔS_m; in the case of polymeric materials, however, low melting points are generally due to relatively large entropies of fusion.[39] The low melting point reported for poly(trimethylene oxide) is thus consistent with a high degree of conformational disorder in the molten state, where the polymer chains are also in their random coil, unperturbed states.[6,21,22,40,41] Such randomness would of course be associated with an unusually large configurational entropy for the amorphous chain molecule, and therefore with a correspondingly large value of ΔS_m and a relatively small value of T_m. This correlation between the melting point of the crystalline polymer and the unperturbed dimensions it exhibits in the random coil state may in fact apply to the polyoxyalkanes in general. As shown in Figure 6, the melting points[38] of members in the $[(CH_2)_y\text{-O-}]_x$ series vary with y in a manner strikingly similar to that shown by the characteristic ratio in Figure 5.

Acknowledgments. Y.T. wishes to thank the Ministry of Education of Japan for the Fellowship provided during his visit to the University of Michigan in 1974–1975. J.E.M. wishes to acknowledge financial support in general from the National Science Foundation of the United States.

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Nuclear Magnetic Resonance Studies on Pyridine Dinucleotides. 4.[1] Measurements of Correlation Times and the Binding of Oxidized Nicotinamide Adenine Dinucleotide and Adenosine 5′-Monophosphate to Lactate Dehydrogenase as Viewed by ^2H and ^{13}C Relaxation Times

Albert P. Zens, Patricia T. Fogle, Thomas A. Bryson, R. Bruce Dunlap,
Ronald R. Fisher, and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina,
Columbia, South Carolina 29208. *Received June 2, 1975*

Abstract: By employing the method of Saito, Mantsch, and Smith, deuterium quadrupole coupling constants have been experimentally determined for NAD$^+$ and several purine ring systems. From a combination of ^{13}C T_1 determinations and ^2H line widths, the reorientational correlation times can be extracted from the well-known equations. The trends in the correlation times among the purines are discussed in terms of intermolecular interactions. As an application of this aproach, the binding of NAD$^+$ and 5′-AMP to M_4LDH was studied by observing the line widths of the ^2H and ^{13}C resonances of the nucleotides. Because both ligands were found to be undergoing rapid exchange with the protein, M_4LDH, their correlation times could be inferred from the line width data. It was concluded that NAD$^+$ binds differentially to the protein M_4LDH in the absence of a substrate. That is, the adenine portion of NAD$^+$ was found to have a longer correlation time when bound to the enzyme than the analogous correlation time for the pyridyl ring. The advantages of using ^2H Fourier transform NMR methods in studies of ligand binding to enzyme are briefly discussed.

With the advent of experimental techniques that allow the resolution of the contribution of proton j to the spin–lattice relaxation time of proton i,[2-4] relaxation methods are potentially a powerful probe with regard to the solution conformational dynamics of complex molecules. Reference to eq 1 illustrates this fact, i.e., one can calculate a conformationally averaged interatomic distance between atoms i and j without recourse to molecular theories of structure and bonding. This,