A Comparison of the Intrinsic Viscosities of Oligomeric Propylene Glycols with the Behavior Predicted for Models in Aqueous Solution at 25°

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ABSTRACT: Intrinsic viscosities of the oligomeric propylene glycols in water agreed well with $[\eta]$ values computed for a Stuart–Briegleb model chain folded spirally into a tightly coiled disk with most of the hydrophobic methyl groups in the center of the coil. Expanded models such as a loosely folded rod, doughnut, or flexible coil gave values of $[\eta]$ for the 16-mer which were considerably higher than experiment.

In a recent investigation of the hydrodynamic properties of the cellodextrins in aqueous solution, Ihnat and Goring concluded that the short chain oligomers of cellulose were essentially rodlike in configuration.[1] The present work represents an extension of their study on stiff, hydrophilic chains to an analysis of the viscometric behavior of flexible, hydrophobic chains in water. Polypropylene glycol (PPG) oligomers were chosen because it was anticipated that the conformation of the chain would be strongly influenced by hydrophobic interactions between the side-chain methyl groups.[2]

Computational Methods

The essential feature of the analysis was to compare the intrinsic viscosities of the polypropylene glycols in water with the intrinsic viscosities derived for Stuart–Briegleb atom models of various conformation. The intrinsic viscosity of the model $[\eta]_m$ was computed from the Einstein–Simha equation[3,4] in the form

$$[\eta]_m = \nu H v \tag{1}$$

where ν is the Simha viscosity increment, H is a specific volume hydration factor, and v is the specific volume of the solute. Values of ν, H, and v appropriate to various model shapes were calculated as described in the following sections.

1. Disk-Coil. An examination of the molecular models showed that the polypropylene glycol chain was indeed very flexible and could be bent into a flat, compact coil at chain lengths as short as five repeating units. This "disk-coil" arrangement had a micelle-type structure with most of the side-chain methyl groups close packed in the interior of the coil (Figure 1). These characteristics were also retained in models with fewer than five repeating units, although it was not possible to form a complete coil with the ends meeting. As a working approximation the disk-coil was assumed to have an oblate ellipsoidal shape.

For oligomeric chains of degree of polymerization (D.P.) up to 17, the axial ratio of the disk-coil, $[a/b]_m$, was computed from the dimensions of the model by the equation

$$\left[\frac{a}{b}\right]_m = \frac{W_1 + W_2}{2T} \tag{2}$$

where W_1 and W_2 are two plane perpendicular diameters and T is the average thickness of the model. Values of ν corresponding to $[a/b]_m$ were then derived from Scheraga's tables.[5]

The method of calculating the hydration of the disk-coil model was similar to that used by Ihnat and Goring.[1] A hydration factor was computed for dipropylene glycol and this value of H was then considered to apply to all the oligomer disk-coil models. The monomer, propylene glycol, was rejected for this purpose because of its small volume (73.4 ml mol^{-1}) when compared with the water molecule. Also, the monomer is the oligomer which is least representative of the polypropylene glycol chain structure.

An examination of the molecular model revealed that the dimer could assume two extreme configurations. One was an extended, rodlike form which could be approximated in shape by a prolate ellipsoid with an axial ratio of 1.63. This gave a value of $H = 1.32$. The other configuration was compact and nearly spherical ($[a/b]_m = 1.0$) leading to a factor $H = 1.42$. Results for the disk-coil models using both values of H are employed in the ensuing viscometric comparisons.

It is interesting to note that the hydrations determined as above correspond to a range of 0.31–0.41 ml of water per gram of oligomer, which is close to the viscometric hydration associated with some common nonionic surfactant micelles.[6] Furthermore, the hydration factors obtained are equivalent to a range of from 1.1 to 1.5 water molecules per propylene oxide unit, in fair agreement with the viscometrically determined result of two water molecules per ether oxygen for short polyoxyethylene chains[7] and for some model ether compounds.[8]

For the calculation of both the hydration factor and $[\eta]_m$ for the disk-coils, v was taken to be the specific

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(1) M. Ihnat and D. A. I. Goring, *Can. J. Chem.*, **45**, 2353 (1967).

(2) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).

(3) (a) A. Einstein, *Ann. Physik.*, **19**, 289 (1906); (b) *ibid.*, **34**, 591 (1911).

(4) R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

(5) H. A. Scheraga, *J. Chem. Phys.*, **23**, 1526 (1955).

(6) W. L. Courchene, *J. Phys. Chem.*, **68**, 1870 (1964).

(7) M. Rösch, *Kolloid-Z.*, **147**, 78 (1956).

(8) H. Schott, *J. Chem. Eng. Data*, **11**, 417 (1966).

volume of the pure glycol computed for a particular D.P. from eq 13.

As later shown, the disk-coil proved to be the conformation most likely to apply to the real chain. Therefore calculations of $[\eta]_m$ were made over the D.P. range from 2 to 17. A similar range was covered for the calculations of $[\eta]_m$ for the flexible coil model. For the geometric models shown in Figure 2, $[\eta]_m$ was determined only for a D.P. of 16, corresponding to the molecular weight of the highest oligomer studied.

2. Stiff Rod. In this model, as well as in the other configurations in Figure 2, a uniform hydration layer of bound water (represented by the dashed outlines in Figure 2) was considered to be an integral part of the hydrodynamic unit. The thickness of the layer was computed as the thickness of a uniform hydration shell around the dimer molecule in its compact, spherical configuration. Using a hydration factor of 1.42, the resulting increment in the radius of the dimer due to the hydration layer worked out to be 0.47 Å, to give H = 1.45 for the 16-mer stiff rod.

The unhydrated length, l, and the average unhydrated diameter, d, of the 16-mer stiff rod were 65.3 and 5.67 Å, respectively. The axial ratio of a prolate ellipsoid equivalent to the hydrated rod was calculated from the relation[9]

$$\left(\frac{a}{b}\right)_m = 0.817\left(\frac{l + 0.94}{d + 0.94}\right) \qquad (3)$$

3. Loosely Folded Rod. The hydrodynamic particle was assumed to consist of the 16-mer rod and its layer of bound solvent, together with solvent molecules which were "trapped" between the angular sections of the rod.[10] The contained angles were set at 30° and each section was assigned a length of $[l/3 + 0.94]$ Å. The over-all hydrodynamic envelope was represented by an oblate ellipsoid with minor axis $(d + 0.94)$ and an axial ratio of 5.04. From the volume of the ellipsoid, a value of H = 2.44 was obtained.

4. Doughnut. The solvent in the hole was assumed to be hydrodynamically immobilized. The circumference of the doughnut at its midsection was set equal to l. The model was then approximated by an oblate ellipsoid with

$$\left[\frac{a}{b}\right]_m = \left(\frac{l}{\pi} + d + 0.94\right)\Big/(d + 0.94) \qquad (4)$$

The hydrated volume was computed as the volume of a cylinder of diameter $[(l/\pi + d + 0.94)$ and length $(d + 0.94)$, which resulted in a value of H = 2.48.

5. Tightly Folded Rod. This model was also represented as an oblate ellipsoid with minor axis $(d + 0.94)$ and major axes W_1 and W_2 given by

$$W_1 = \left(\frac{l}{3} + 0.94\right) \qquad (5)$$

$$W_2 = (3d + 0.94) \qquad (6)$$

To determine the hydrated volume, the central section of the model was represented by an oblong box of length W_1, height $(d + 0.94)$, and width $2d$. The two edges of the model were each represented by semicylinders of length W_1 and radius $(d + 0.94)/2$. The resulting value for the hydration factor was 1.58.

6. Peterlin Flexible Coil. Peterlin's hydrodynamic theory for short chains[11,12] was applied to the experimental results. In his treatment, several theoretical curves of $[\eta]_{rel}$ *vs.* D.P. were derived, each one corresponding to a necklace model defined by two parameters, one for the monomer unit hydrodynamic interaction and the other representing the chain flexibility; $[\eta]_{rel}$ is given by

$$[\eta]_{rel} = [\eta]_n/[\eta]_0 \qquad (7)$$

where $[\eta]_n$ is the intrinsic viscosity of the necklace model of D.P. = n and $[\eta]_0$ is the intrinsic viscosity of the smallest unit (single bead) of the chain.

A computer curve-fitting program gave the $[\eta]_{rel}$ *vs.* D.P. curve which agreed best with the experimental data. The best fit curve corresponded to the limiting model of maximum hydrodynamic interaction and maximum chain flexibility. Pictorially this could be represented as an extremely flexible chain made up of a series of touching elementary spheres.

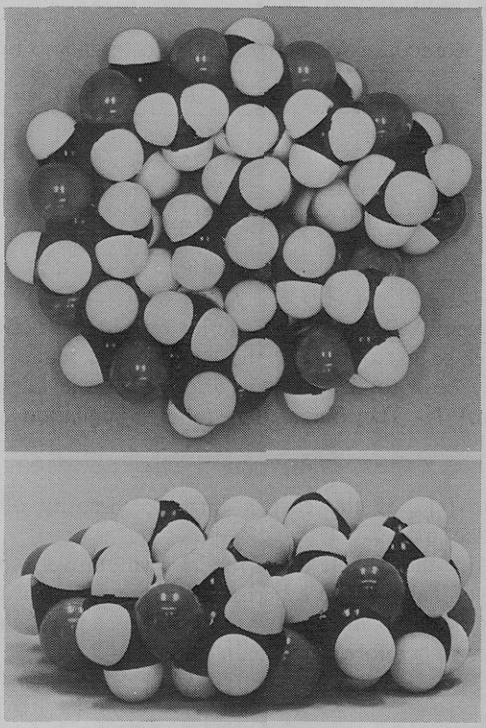

Figure 1. Photograph of the polypropylene glycol disk-coil model of D.P. 12.

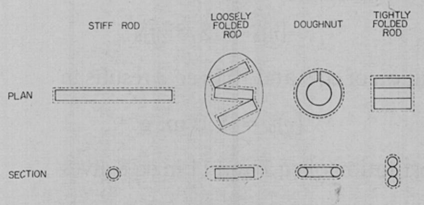

Figure 2. Geometric models of the polypropylene glycol 16-mer chain.

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(9) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley & Sons, Inc., New York, N. Y., 1961, p 342.

(10) See ref 9, p 337.

(11) A. Peterlin, *J. Chim. Phys.*, **47**, 669 (1950).

(12) A. Peterlin, *J. Polym. Sci.*, **8**, 173 (1952).

TABLE I
MOLECULAR WEIGHTS, SPECIFIC VOLUMES, AND INTRINSIC VISCOSITIES OF POLYPROPYLENE GLYCOLS IN WATER AT 25°

Glycol	$\overline{M}_n$	Av D.P.	v, ml g^{-1}	$[\eta] \pm$ S.D., ml g^{-1}	k'
Di	130	1.93	0.982	3.48 ± 0.020	0.83
Tri	175	2.7	0.987	3.67 ± 0.016	0.78
Penta	291	4.7	0.992	4.01 ± 0.050	0.85
P400	313	5.1	0.994	4.11 ± 0.006	0.88
425	410	6.8	0.994	4.31 ± 0.039	0.93
1025	940	15.9	0.999	5.52 ± 0.028	0.52

Recently, Bianchi and Peterlin revised the necklace model so as to include the contribution made by a single bead to the intrinsic viscosity of the oligomer chain.[13,14] They obtained the following equation

$$[\eta]_{\text{cor}} = [\eta]_0 + [\eta]_n \qquad (8)$$

where $[\eta]_{\text{cor}}$ is the correct intrinsic viscosity of the necklace model.

To fit the flexible chain model quantitatively to the data of Table I, the experimental intrinsic viscosity of the dimer (3.5 ml g^{-1}) was selected as a normalizing point. Therefore, for a chain of D.P. = 2

$$[\eta]_{\text{cor}} = 3.5 \text{ ml g}^{-1} \qquad (9)$$

The theoretical value of $[\eta]_{\text{rel}}$ for the dimer was determined as 2.5 ml g^{-1} from Peterlin's data.[15] Thus, for D.P. = 2, from eq 7

$$[\eta]_n = 2.5\,[\eta]_0 \qquad (10)$$

Substitution of eq 9 and 10 in eq 8 results in

$$[\eta]_0 = 1.0 \text{ ml g}^{-1} \qquad (11)$$

and substitution of eq 7 and 11 in eq 8 gives

$$[\eta]_{\text{cor}} = 1.0 + [\eta]_{\text{rel}} \qquad (12)$$

Values of $[\eta]_{\text{rel}}$ over the D.P. range from 3 to 16 were read off from Peterlin's curve corresponding to the flexible coil model described above.[16] $[\eta]_{\text{cor}}$ was then determined for each D.P. from eq 12.

Experimental Section

Dipropylene glycol and tripropylene glycol samples were generously donated by the Dow Chemical Co., Midland, Mich. We are particularly indebted to Dr. B. Weibull of Mo Do Aktiebolag (Sweden) for preparing and fractionating the pentapropylene glycol sample. PPG P400 was purchased from Matheson Coleman and Bell Co., while PPG 425 and 1025 samples were obtained from the J. T. Baker Chemical Co. These polyglycols were of the best grade commercially available and were used without further purification for the viscosity measurements. Number average molecular weights were determined by vapor pressure osmometry (Mechrolab Model 301 A) in isopropyl alcohol at 37°. The calibration standard was propionamide.[17]

The densities of the pure polyglycols at 25° were determined by volume dilatometry, the details of which are given elsewhere.[18]

Viscosities were measured in Ubbelohde viscometers designed to make kinetic energy corrections negligible.[19] Water flow times were about 150 sec and the average shear rate for these systems was 650 sec^{-1}. Temperature control at 25 ± 0.01° was provided by a Townson and Mercer bath.

Water and all solutions were filtered directly into the viscometers through fine millipore filters (1-μ pore size or less) in Swinny hypodermic adapters fitted to hypodermic syringes. At least five flow times were measured for each solution and reproducibility was usually within ±0.1 sec.

The small differences between the densities of the solutes and the solvent resulted in negligible density corrections to the viscosity data.

Results

The primary experimental data for the propylene glycol oligomers are given in Table I. The average degrees of polymerization are estimated from the number average molecular weights, $\overline{M}_n$. Our confidence in these values seems justified in view of the recent work of Baijal and Blanchard,[20] who showed that low molecular weight ($\leq$2200) polypropylene glycols have narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n \leq 1.1$). For PPG 425 and 1025, these authors determined number average molecular weights of 420 and 920, respectively, which are within 2.5% of the values given in Table I for these compounds.

Also included in Table I are the dry specific volumes, v, which are precise to within ±0.001 ml g^{-1}. In agreement with the findings of Scholtan and Lie,[21] the specific volume was found to be inversely proportional to the molecular weight, $\overline{M}_n$. Our results expressed as an empirical equation give

$$v = 1.0013 - \frac{2.524}{\overline{M}_n} \qquad (13)$$

where v is in milliliters per gram.

Intrinsic viscosities, $[\eta]$, determined from Huggins' plots of the experimental data, are listed together with their standard deviations, S.D. Huggins' constants, k', although not involved in this work, have been included for comparison. Examples of reduced viscosity–concentration plots are shown in Figure 3.

Table II contains the axial ratios and the two sets of theoretical intrinsic viscosities derived from measurements on the oblate ellipsoid disk-coil models. The first set of intrinsic viscosities, $[\eta]_{\text{mc}}$, corresponds to the upper limiting values obtained by using the compact dimer hydration factor, H = 1.42. The second set,

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(13) U. Bianchi and A. Peterlin, *J. Polym. Sci., Part A-2*, **6**, 1759 (1968).

(14) A. Peterlin, *Amer. Chem. Soc., Polym. Preprints*, **9**, 323 (1968).

(15) Reference 14, Figure 5C.

(16) Reference 11, Figure 5, curve with α = 0.

(17) L. S. Sandell, Ph.D. Thesis, McGill University, Montreal, Quebec, 1970.

(18) L. S. Sandell and D. A. I. Goring, to be published.

(19) A. W. Craig and D. A. Henderson, *J. Polym. Sci.*, **19**, 215 (1956).

(20) M. D. Baijal and L. P. Blanchard, *J. Appl. Polym. Sci.*, **12**, 169 (1968).

(21) W. Scholtan and S. Y. Lie, *Makromol. Chem.*, **108**, 104 (1967).

$[\eta]_{me}$, represents the lower limit based on a hydration factor $H = 1.32$ for the extended dimer model. The disk-coil intrinsic viscosities are compared graphically with the experimental values in Figure 4. The upper (full line) and lower (dashed line) boundaries of the hatched area are formed by least-squares lines through the $[\eta]_{mc}$ and $[\eta]_{me}$ values, respectively. The root-mean-square deviation between each set of disk-coil model intrinsic viscosities and its fitted straight line is ± 0.07 ml g^{-1}.

The intrinsic viscosities of the other 16-mer models and of the Peterlin flexible coil are also shown in Figure 4.

Discussion

The results in Figure 4 indicate that the water impermeable disk-coil structure is a good hydrodynamic model for oligomeric polypropylene glycol. The best agreement between experiment and theory is obtained when the viscometric hydration factor is calculated from the most compact form of the dimer model. In this configuration the dimer is almost spherical, with the two methyl groups actually touching to form a hydrophobic bond. Thus the best correlation for the model is obtained when the dimer itself tends toward a hypercoiled state.

The disk-coil model can be justified from a thermodynamic standpoint by assuming that hydrophobic bonds between the close-packed methyl groups play a major role in the stabilization of the structure. The importance of hydrophobic forces in determining molecular conformation in aqueous solution has been shown by many workers in different fields.[22–29] These effects may show up in unusual hydrodynamic behavior, as in the work of Eliassaf.[30] He found, from intrinsic viscosity data, that poly(methacrylic acid) had a shorter statistical chain element than poly(acrylic acid) in spite of the stiffening effect of the methyl side groups. This discrepancy was attributed to the ability of poly(methacrylic acid) to undergo intramolecular hydrophobic bonding through the methyl side group; poly(acrylic acid) has no hydrophobic side group. Similarly, hydrolyzed copolymers of maleic anhydride and *n*-butyl vinyl ether exist in a compact, hypercoiled state because of the hydrophobic interactions between the side-chain butyl groups.[31]

TABLE II

AXIAL RATIOS AND INTRINSIC VISCOSITIES OF DISK-COIL MODELS

D.P.	$\left[\frac{a}{b}\right]_m$	$[\eta]_{mc}$, ml g^{-1}	$[\eta]_{me}$, ml g^{-1}
2	1.0	3.48	
3	1.50	3.67	3.41
5	1.94	3.97	3.69
7	2.28	4.25	3.95
10	2.78	4.67	4.34
12	3.17	5.00	4.64
15	3.44	5.25	4.87
17	3.61	5.40	5.02

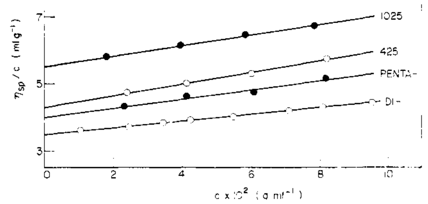

Figure 3. Plots of reduced viscosity *vs.* concentration for some of the oligomers.

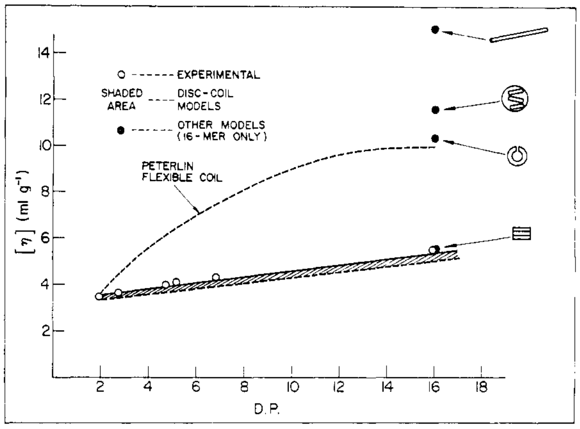

Figure 4. A plot of [η] *vs.* D.P. for the propylene glycol oligomers and for the various models in aqueous solution at 25°.

Among the models in Figure 2, the only configuration which fits the experimental result well is the rod tightly folded in three sections. This model resembles the disk-coil in that it is flat and has a high packing density. However, such a conformation is improbable because of the sharp bends required. The other models of more open structure have intrinsic viscosities which are too high. The stiff rod model is greatest in error, in contrast to the behavior of the cellodextrins for which the rod model is in agreement with the experimental results.[1] The loosely folded rod might be considered to correspond very approximately to a random coil. Its high intrinsic viscosity shown in Figure 4 suggests that the random coil model is inappropriate for the propylene glycol oligomers dissolved in water.

In the Peterlin flexible coil model, [η] is found to have a dependence on chain length which is too strong in the low D.P. range. Above a D.P. of 10 however, the Peterlin curve levels off to a slope which approxi-

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(22) G. Némethy and H. A. Scheraga, *J. Phys. Chem.*, **66**, 1773 (1962).

(23) C. Tanford, P. K. De, and V. G. Taggart, *J. Amer. Chem. Soc.*, **82**, 6028 (1960).

(24) G. D. Fasman, C. Lindblow, and E. Bodenheimer, *ibid.*, **84**, 4977 (1962).

(25) N. Lotan, A. Yaron, and A. Berger, *Biopolymers*, **4**, 365 (1966).

(26) D. C. Poland and H. A. Scheraga, *J. Phys. Chem.*, **69**, 2431 (1965).

(27) A. M. Liquori, G. Barone, V. Crescenzi, F. Quadrifoglio, and V. Vitagliano, *J. Macromol. Chem.*, **1**, 291 (1966).

(28) G. Barone, V. Crescenzi, B. Pispisa, and F. Quadrifoglio, *ibid.*, **1**, 761 (1966).

(29) For a general review of hydrophobic interactions, see G. Némethy, *Angew. Chem. Intern. Ed. Engl.*, **6**, 195 (1967).

(30) J. Eliassaf, *Polym. Lett.*, **3**, 767 (1965).

(31) P. Dubin and U. P. Strauss, *J. Phys. Chem.*, **71**, 2757 (1967).

mates that of the disk-coil model. It is interesting to note that the flexible coil value of $[\eta]$ for the 16-mer is relatively close to that of the doughnut and loosely folded rod models.

The disk-coil thus appears to be the best approximation to the conformation of the glycols in water. However, this model can only be significant from the point of view of a time average. In reality, rapid Brownian motion will cause the flexible chain to assume an infinite variety of shapes. The results suggest that the chain exists for a high proportion of the time in a flat, tightly coiled configuration.

Solvent-Induced Conformational Expansion of Oligomeric Propylene Glycols

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ABSTRACT: The relative expansion of the oligomeric propylene glycol chain was determined viscometrically in six varied solvents at 25°. The ratio of the intrinsic viscosity of the 16-mer to that of the dimer ($[\eta]_{16}/[\eta]_2$) was found to be low (1.6) in high dielectric constant solvents like water and 6 *M* aqueous urea, indicating that the 16-mer chain is in a tightly coiled state in such media. In benzene, $[\eta]_{16}/[\eta]_2$ increased to 2.5, which suggests that the oligomer chain opens up to a looser Gaussian coil configuration in hydrophobic solvents.

In a previous paper it was suggested that oligomeric propylene glycols in water exist in a solvent impermeable, disk-coil configuration stabilized by side-chain hydrophobic interactions.[1] This model, however, can only be valid in aqueous solutions.[2,3] In organic solvents, in which hydrophobic bonding cannot occur, the conformation of the oligomer chain would depend on the nature of the solute–solute and solute–solvent van der Waals forces. Conceivably, in a favorable solvent environment the tightly packed coil would tend to open up to a more extended conformation. Thus, it was of interest to determine the expansion of the polypropylene glycol (PPG) chain in various solvent systems, relative to its conformation in water.

The ratio of the intrinsic viscosity of the 16-mer to that of the dimer, $[\eta]_{16}/[\eta]_2$, was taken as a measure of the relative expansion of the coil. The justification for this is based on the premise that for a relatively long, flexible chain like the 16-mer, expansion produces a decrease in the segment density and therefore an increase in the hydrodynamic specific volume of the solute. A small essentially rigid molecule such as the dimer is not expected to show such conformational changes. If it is assumed that the solvation of the chain is the same for the dimer and the 16-mer in a given solvent, then an increase in the ratio $[\eta]_{16}/[\eta]_2$ over that in water could reflect a transition from the compact disk-coil to a more expanded conformation. It should be noted that this procedure is most effective when the 16-mer (the largest oligomer soluble in water at room temperature) is compared with the dimer. Comparison of the viscosity of shorter oligomers with that of the dimer would be expected to give smaller changes which would be more difficult to detect.

TABLE I
APPARENT SPECIFIC VOLUMES OF DIPROPYLENE GLYCOL AND PPG 1025 AT 25°

Oligomer	Solvent	Concn, g ml^{-1}	$\bar{v}$, ml g^{-1}
Dipropylene glycol	Benzene	0.0508	0.994
	Tetrahydropyran	0.0497	0.987
	Methanol	0.0499	0.948
PPG 1025	Benzene	0.0524	0.992
	Tetrahydropyran	0.0502	0.996
	Methanol	0.0496	0.961

Experimental Section

Details on the dipropylene glycol and PPG 1025 (16-mer) samples are given in a previous report.[1] Benzene, methanol, and dimethyl sulfoxide (DMSO) were reagent grade solvents and tetrahydropyran (THP) was technical grade.

Solution densities at 25° were required for the determination of intrinsic viscosities. Densities of dipropylene glycol and PPG 1025 in benzene, tetrahydropyran, and methanol were measured in 5-ml Lipkin pycnometers at an average concentration of 0.05 g ml^{-1}. Apparent specific volumes, $\bar{v}$, computed by Kraemer's formula[4] were then used to calculate correction factors for the reduced viscosity–concentration plots.[5] For the DMSO and 6 *M* aqueous urea solutions the corrections were negligible because of the small differences between the densities of the solutes and solvents. Intrinsic viscosities were measured at 25 ± 0.01° by the techniques described previously.[1]

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(1) L. S. Sandell and D. A. I. Goring, *Macromolecules*, **3**, 50 (1970).

(2) G. Némethy, *Angew. Chem. Intern. Ed. Engl.*, **6**, 195 (1967).

(3) G. Némethy, H. A. Scheraga, and W. Kauzmann, *J. Phys. Chem.*, **72**, 1842 (1968).

(4) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," The Clarendon Press, Oxford, 1940, p 60.

(5) M. Ihnat, A. Szabo, and D. A. I. Goring, *J. Chem. Soc., A*, 1500 (1968).